A.A. YAROSLAVTSEV

PROBLEMS AND EXERCISES IN ANALYTICAL CHEMISTRY

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THEORETICAL FOUNDATION OF MODERN CHEMICAL ANALYSIS

Yu. LYALIKOV, D.Sc.
and Yu. KLYACHKO, D.Sc.

This monograph deals with the basic principles of the unified modern theory of chemical qualitative analysis of inorganic substances. Offers analytical classifications of ions according to their solubility, ability to form colour substances, extractability, chromatographic and electrochemical characteristics, etc. Describes methods of concentrating, masking and separating the ions and molecules being determined. A separate chapter is devoted to methods of qualitative analysis of natural and industrial materials.

The book is intended for a wide circle of analytical chemists, chemistry teachers, post-graduates, and students majoring in the field of analytical chemistry.

GENERAL CHEMISTRY

N. GLINKA, D.Sc.

This book has enjoyed wide popularity for years in the Soviet Union and elsewhere. It is intended mainly for higher-school chemistry students. Offers a systematic exposition of the theoretical problems of general chemistry and extensive reference material. The present edition (translated from the 20th Russian edition published in 1978) has been considerably revised, the opportunity being taken of making many important additions to the text and bringing the contents thoroughly up-to-date. Special attention is paid to the structure of atoms and molecules, the regularities governing the occurrence of chemical reactions, and redox connection with the introduction of SI units.

LOW-TEMPERATURE PROPERTIES OF POLYMERS

I. PEREPECHKO, D.Sc.

This monograph deals systematically with the properties of polymers at low temperatures. It studies thermal, acoustic, dielectric properties of polymers and the nuclear magnetic resonance. Most sections of the book have been written from the point of view of modern solid-state physics. The book is intended for scientific workers studying physical properties of polymers at low temperatures, for engineers in plastic industry and for teachers and students of physical and chemical institutes.

A.A. YAROSLAVTSEV

PROBLEMS AND EXERCISES IN ANALYTICAL CHEMISTRY

Translated from
the Russian
by
Alexander Rosinkin

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А. А. Ярославцев

Сборник задач и упражнений по аналитической химии

Москва
«Высшая школа»

ИЗДАТЕЛЬСТВО
МИР

FOREWORD

In collecting the problems and exercises for this book we followed the main pedagogical principle: from the simple to the complex. The problems contain examples of calculations which the future analyst will meet in his every-day work in the laboratory of a chemical plant, metallurgical enterprise and in other branches of industry. The answers to the problems were found on calculating machines. Using four-place tables of logarithms and irrational calculating techniques, the student may find his answers differ slightly from those given at the end of the book, but the difference should not exceed $\pm$ 0.0005.

In order to facilitate the use of the book both at home and in the classroom, the author presents the problems in two versions; even-numbered problems are variants of the odd-numbered ones preceding them.

The author takes this opportunity to express his deepest gratitude to V. S. Kalinina for her assistance in selecting the problems in several sections and for helping with the calculations.

Anatoly A. Yaroslavtsev

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INTRODUCTION

Mathematical calculations are the final stage in chemical analysis. However experienced and accurate in carrying out the analytical procedure the analyst may be, the final result, after much tedious and time-consuming work, can be marred down by a single error in calculation. The analyst should therefore remember that *an error in calculation is equivalent to an error in the analytical procedure.*

Calculations. For efficient mathematical calculations, the following mathematical concepts, definitions, and rules should be learned first*.

Number is an expression of quantity. Numbers are classified as accurate and approximate. An accurate number is the result of the counting of a small number of objects or the result of calculations where only accurate numbers are used. In practice accurate numbers rarely occur.

Examples of accurate numbers are the results of determinations, small weights of analytical substances and reagents, smaller units into which larger units are divided (a litre into 1000 ml, an hour into 60 minutes, etc.); the atomic and the equivalent mass of carbon ^{12}C in the atomic mass scale. An approximate number does not give an accurate expression of a quantity, but describes it only approximately, to a certain degree of accuracy. An example is measuring a mass or a volume. The result of calculations where only approximate (or approximate and accurate) numbers are used, is an approximate number as well. An approximate number is property given only when its degree of accuracy is specified.

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* For more details see the book by V. M. Bradis, *How to Calculate?*, Prosveshchenie, Moscow, 1965 (in Russian).

The accuracy of a number is determined by the number of decimal places or significant figures. *Decimal places* are figures standing on the right of the point separating the whole part of the number from its fractional part. For example, the number 25.304 has three decimal places, 10.00008 five decimal places and 734.00, two decimal places.

Significant figures of an approximate number are all figures except zeros standing on the left-hand side and those zeros on the right-hand side which represent figures which are unknown or have been deleted in rounding. All zeros standing in the middle of a number are significant figures. For example, in 230.908 all six figures are significant; in 0.00014, only two, and in 167.0000, three figures are significant. In the last case, all seven figures are significant if the number is known to be accurate. In other words, zeros can be significant only in accurate whole numbers or in the accurate part of an approximate number.

In approximate numbers a distinction is made between authentic and unauthentic figures. As we record the readings from a correct instrument, readings corresponding to the divisions of scale are considered authentic, while the readings falling between two divisions are unauthentic. As we round an accurate number we make it approximate and its last significant figure becomes unauthentic. For example, if we round the accurate number 249 to 250, the new number becomes approximate; the figure 2 remains authentic, while the figure 5 is unauthentic. In the results of calculations only those figures are authentic which are obtained by processing authentic figures. All other figures are unauthentic. The result of a calculation can be considered correct if only its last figure is unauthentic, while an instrument reading can be regarded as correct only if it contains one unauthentic figure (the 'eye' reading). The *accuracy of the result of a calculation cannot be higher than the accuracy of the least accurate number involved in the calculation....* The least accurate number is the one containing the *least* number of significant figures (multiplication and division) or decimal places (addition and subtraction).

It makes sense to attempt calculations only with numbers of equal accuracy. Before starting a calculation, it is therefore necessary to find the least accurate number and round

all other numbers so, that they contain one significant figure more ('spare') than the least accurate number. The following rule should be followed in rounding: if the first figure to be deleted is 5 or greater, the preceding figure should be increased by one unit. If the first figure to be deleted is less than 5 the remaining figures are not changed. In the addition or subtraction of mixed decimals, the number given to the least number of decimal places is considered the least accurate. Calculations are continued until a 'spare' figure is obtained which is then omitted and the last remaining figure rounded. The number of significant figures (multiplication or division) or decimal places (addition and subtraction) in the final result must be equal to the number of significant figures in the least accurate number involved in the calculation.

If the data in a calculation are highly accurate, but only an approximate result is required, all initial data are rounded so that they contain one significant figure (or a decimal fraction) more than required in the result. *One should not calculate to a degree of accuracy greater than required.*

If an approximate calculation is done to a high degree of accuracy, the sign = (equals) is placed before the result. If the accuracy is low, the sign $\approx$ (equals approximately) is used. *Calculations done without observing these rules will be incorrect.*

Calculation techniques. Calculations can be performed (1) by mental arithmetic, (2) by combining mental and written arithmetic, (3) by written calculation alone, (4) using a slide rule, various tables, graphs, nomograms, etc., and (5) using a calculating machine. Mental arithmetic, mental and written calculations, and calculations with a slide rule are suitable only for approximate calculations. The multiplication and division of large numbers to a high degree of accuracy should be performed with tables of logarithms or on a calculator. Ordinary written calculations can only be used to (1) add and subtract large numbers; and (2) multiply and divide large numbers by numbers consisting of only one figure or containing one significant figure other than unity. When using a calculator, it is necessary to round all results (final and intermediate) in accordance with the above rules. *Never use your own written calculations*

to multiply or divide large numbers, especially if there are several unauthentic figures.

When solving an analytical problem, never determine the numerical values of all the intermediate results. It is quite sufficient to devise a formula for each operation, to substitute the required values into it, and to designate the result by a letter, which is then treated as a numerical value in further operations. When it comes to the final operation, write out the general formula, cancel wherever necessary, find logarithms and use logarithm tables to determine the final result. While doing calculations, write out all operations neatly and arrange them in strict order. Write legibly. When adding or subtracting, it is especially important to write the numbers one under another so that all the figures fall into right columns. The use of squared paper facilitates this purpose.

Draw a vertical line one third of the way across the page and write down the problem, all the auxiliary data taken from tables, and perform all operations on the wider part of the page. All calculations should be done in the margin. This will prevent possible errors, the solution can be more quickly checked, and the need for rough paper is removed. Examples of such calculations are given by way of illustration.

All data in the first problem are of very low accuracy (to one significant figure) and all auxiliary data should be rounded to two significant figures. As for the result, only one significant figure should be left in it, since the accuracy of the result cannot be higher than the accuracy of the least accurate number used in the calculations. In other words, we can only say that about 10 ml of H_2SO_4 are required, and the sign $\approx$ (equals approximately) rather than the sign of equality (=) should therefore be put before the result. This example shows that the solution of the problem is much simpler if we follow the rules. The problem can be solved even faster if we use a slide rule or a calculator. True, a slide rule imposes limitations on the accuracy (to two or three significant figures only).

When performing calculations, remember that an error can be the result of inattentive rewriting. Therefore, avoid rewriting wherever possible. For example, while solving the

Wider part of the page | Margin

Problem No... . How many millilitres of 50% H_2SO_4 are required to neutralize a solution of 9 g of potassium hydroxide?

Auxiliary data:

	from table	rounded
Mol. mass of H_2SO_4	98.08	98
Mol. mass of KOH	56.11	56
Density of 50% H_2SO_4	1.395	1.4

Reaction equation

$$2KOH + H_2SO_4 = K_2SO_4 + 2H_2O$$

Solution.

1. How many grams of anhydrous H_2SO_4 are required to neutralize 9 g of KOH?

$2KOH - H_2SO_4$

$2 \times 56 - 98$ $\qquad x = \dfrac{9 \times 98}{2 \times 56} = a$ g

$9 - x$

$98 \times 9 = 882 \approx 880$

2. How many grams of 50% H_2SO_4 are required for the same purpose?

$50 - 100$

$a - y$ $\qquad y = \dfrac{a \times 100}{50} = b$ g

$$\begin{array}{r} 56 \\ \times\ 1.4 \\ \hline 22.4 \\ +\ 56 \\ \hline 78.4 \end{array}$$

3. What is the volume of b g of a 50% solution of H_2SO_4?

1000 ml — 1400 g

z ml — b g $\qquad z = \dfrac{1000 \cdot b}{1400} =$

$$= \frac{b}{1.4} = c \text{ ml};$$

$$c = \frac{9 \times 98 \times 100}{2 \times 56 \times 50 \times 1.4} = \frac{882}{78.4} \approx \frac{880}{78} \approx$$

$$\approx 10 \text{ ml}$$

$$\begin{array}{r|l} & 11 \\ 78 & 880 \\ & 78 \\ \hline & 100 \\ & 78 \\ \hline & 22 \end{array}$$ (remainder)

Problem No... . Calculate as accurately as possible the number of millilitres of a 50% solution of H_2SO_4 required to neutralize 9.000 g of pure KOH.

Wider part of the page	Margin
Auxiliary data: Mol. mass of H_2SO_4 98.08 Mol. mass of KOH 56.11 Density of a 50% solution of H_2SO_4 1.395	
Reaction equation: $2KOH + H_2SO_4 = K_2SO_4 + 2H_2O$	
Solution.	
1. How many grams of anhydrous H_2SO_4 are required to neutralize 9.000 g of KOH? $2KOH - H_2SO_4$ $2 \times 56.11 - 98.08$ $9.000 - x$ $x = \frac{9.000 \times 98.08}{2 \times 56.11} = a$ g.	
2. How many grams of a 50% solution of H_2SO_4 are required for the same purpose? $50.00 - 100$ $a - y$ $y = \frac{a \times 100}{50.00} = b$ g.	$\log 56.11 = 1.7491$ $+$ $\log 1.395 = 0.1446$ 1.8937
3. What is the volume, in ml, of b g of a 50.00% solution of H_2SO_4? 1000 ml — 1.395 g z ml — b g $z = \frac{1000 \times b}{1.395} = \frac{b}{1.395} = c$ ml; $c = \frac{9.000 \times 98.08 \times 100}{2 \times 56.11 \times 50.00 \times 1.395} = 11.27$ ml	$\log 9.000 = 0.9542$ $+$ $\log 98.08 = 1.9916$ 2.9458 -1.8937 $\log x = 1.0521$ $x = 11.27$

above problem, after cancelling the fraction find the sum of logarithms of the denominator first and then of the numerator. Do not then rewrite but put the first sum directly beneath the second and continue the calculation.

Problems

1. What numbers, accurate or approximate, can be used to express the following: (a) the mass of a body; (b) the number of test tubes on a stand; (c) the number of test tubes in all the laboratories of a plant; (d) the number of seconds in an hour; (e) the number π; (f) an expression of the value of π; (g) the volume of a solution measured out by a cylinder; (h) the volume of a solution measured out by a burette?

2. Which of the following are approximate values: (a) result of analysis; (b) mean result of several parallel analyses of the same sample; (c) Avogadro's number; (d) tabulated densities of acids of various concentrations; (e) logarithm of an accurate number; (f) logarithm of an approximate number; (g) valency of an element; (h) tabulated atomic and molecular masses?

3. Are the following numbers accurate or approximate? (a) sample weight of 0.5674 g; (b) 5 g of sodium chloride weighed out for a test; (c) 1 litre contains 1000 ml; (d) a rod is 50 mm long.

4. Point out which of the following are approximate and which accurate numbers: (a) the atomic mass of ^{12}C is 12; (b) the atomic mass of hydrogen is 1.008; (c) a sample weighs 12.0056 g; (d) three tests have been carried out.

5. How do we write down the weight of 8 g of a substance as measured on a technical, chemical, and analytical balance?

6. Ten millilitres of a solution are measured into three flasks using a 1-litre volumetric cylinder for one flask, a 25-ml volumetric cylinder for another, and a 50-ml burette for the last. Write down the volume of the solution in each flask.

7. Round 25.9352 to an accuracy of 5, 4, 3, and 2 significant figures.

8. The mass of water contained in a 1-litre volumetric flask is 0.99717 kg at 20 °C. Round this number to 4, 3, and 2 significant figures.

9. How many significant figures and decimals are there in the following: (a) 20.0008; (b) 0.0025; (c) 987.500?

10. How many significant figures and decimals are there in the following approximate numbers: (a) 900; (b) 0.2005; (c) 5.4000; (d) 1.008?

11. Two samples each weighing 1.5 g were used to prepare 150 ml of salt solutions. One sample was weighed out on a technical balance whose accuracy is 0.1 g; the other on an analytical balance. How many grams of salt are contained in 50 ml of each solution?

12. A piece of wire, 25.0 cm long, is measured out with an accuracy of 0.1 cm. Determine the length of a one third part of the wire.

13. Round the accurate number 2090 to the nearest hundred. Determine the number of significant figures in this number before and after rounding.

14. A weighing box containing a sample weighs 25.0950 g. Is this number accurate or approximate? How many significant figures does it contain before and after rounding to the nearest hundredth of a gram?

15. An analysis began with 2.2457 g of a reagent. This quantity proved to be insufficient, and a further 0.5248 g and 0.2442 g were added. As the analysis went on, it became necessary to add still another sample of the same reagent. When it was weighed out, the chemical balance read 0.1 g. The mass, as determined on an analytical balance, was not recorded. What was the quantity, in grams, of the reagent used in the analysis?

16. Find the total of the following approximate numbers: 27.9458, 0.4, 2452.35, and 0.0004.

17. When the approximate number 2.5 was divided by an accurate number of 17, the result was 0.1470588. Which figures in the result are unauthentic? What should the result be?

18. An analyst determined the ash content of coal in three parallel tests. The results obtained were: 12.0, 12.2, and 12.3 per cent of ash. He found the mean of the three results: 12.167 per cent. Is the result correct? How should the mean result be written?

19. Round the numbers below and complete the calculation

$$\frac{0.9821 \times 24.36 \times 55.86 \times 500}{25.00 \times 1000 \times 0.9} =$$

(numbers 500 and 1000 are accurate).

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20. Round and calculate the following:

$$\frac{258 \times 0.001 \times 18 \times 0.45}{300.28 \times 0.0091} = \ldots$$

(0.001 is an accurate number).

21. Calculate the following (the result must have the required number of figures):

$$\frac{0.4941 \times 20.23}{18.81} = \ldots$$

22. Calculate as accurately as possible:

$$\frac{0.0016865 \times 1000}{31.607} = \ldots$$

(1000 is an accurate number).

23. What method should be used in the calculations in Problems 19 and 21?

24. What method should be used in the calculations in Problems 20 and 22?

25. Calculate, to an accuracy of two significant figures, what part of a gram-molecule 1 g of aluminium sulphate is.

26. Calculate, as accurately as possible, the number of molecules of copper sulphate contained in 5 g of its crystal hydrate, $CuSO_4 \cdot 5H_2O$, if Avogadro's number is assumed to be 6×10^{23}.

27. Calculate the percentage of aluminium in the crystal hydrate $KAl(SO_4)_2 \cdot 12H_2O$: (a) to an accuracy of one significant figure; (b) to the greatest possible accuracy.

28. Calculate the percentage of water in copper sulphate (blue vitriol): (a) to an accuracy of two significant figures, and (b) to the highest reasonable accuracy.

CHAPTER ONE

GENERAL THEORETICAL PRINCIPLES OF ANALYTICAL CHEMISTRY

A. Concentration of Solutions

The concentration of a solution is the number indicating the quantity of solute contained in a weight or volume unit of solution. The concentration of saturated solutions is usually expressed in grams of an anhydrous substance per 100 g of solvent. This value at a given temperature is constant and is known as *solubility*. There are several ways of expressing concentrations of solutions.

Percent concentration. *The percent concentration of a solution is the number showing the quantity of grams of pure solute contained in* 100 *g of solution.*

Example 1. How many grams of sodium chloride would it take to prepare 80 g of a 5 per cent solution?

Solution. Set out and solve the proportion:

$$\begin{matrix}\text{100 g of solution contain 5 g of NaCl}\\ \text{80 g of solution contain } x \text{ g of NaCl}\end{matrix} \qquad x = \frac{80 \times 5}{100} = 4 \text{ g.}$$

The difference 80 — 4 = 76 g is the mass of solvent required to prepare 80 g of a 5 per cent solution of NaCl using 4 grams of NaCl.

If the weights of solute (a) and solvent (b) are known, the percent concentration of a solution (c%) can be found from the following proportion:

$$\begin{matrix}(a+b) - 100\\ a - x\end{matrix} \qquad x = \frac{a \cdot 100}{(a+b)} = c\ \%$$

Molar concentration. *The molarity of a solution is the number of moles of solute contained in one litre of solution.* In order to determine the molarity of a solution, the num-

ber of grams of solute in one litre of solution is first determined, and this number is then divided by the molecular mass of the solute.

Example 2. Determine the number of grams of $CuSO_4 \cdot 5H_2O$ required to prepare 2 litres of $4M$ solution.

Solution. The molecular mass of $CuSO_4 \cdot 5H_2O$ is 249.69 (see Appendix, Table 1). Round the mass to 250. Set out and solve the following:

(a) 250 g of salt are required to prepare 1 litre of $1M$ solution

x g of salt are required to prepare 2 litres of $1M$ solution

$$x = \frac{2 \times 250}{1} = a \text{ g.}$$

(b) a g of salt are required to prepare 2 litres of $1M$ solution

y g of salt are required to prepare 2 litres of $4M$ solution

$$y = \frac{a \times 4}{1} = \frac{2 \times 250 \times 4}{1 \times 1} = 2000 \text{ g.}$$

Example 3. Determine the molarity of a solution containing 5.0 g of anhydrous sodium sulphate in 150 ml of solution.

Solution. How many grams of salt (a) does one litre of solution contain?

$$a = 5.0 \times 1000/150.$$

Determine the molarity of the solution by dividing this amount by the molecular mass of the sodium sulphate:

$$M = \frac{a}{142} = \frac{5.0 \times 1000}{150 \times 142} = 0.24.$$

Normality. The *normality of a solution is the number of gram-equivalents of solute in one litre of solution.* The normality of solutions is determined as described above, except that gram-equivalents are used instead of molecular masses of solute. When expressing the concentration of a solution in gram-equivalents per litre it is necessary to calculate the equivalent weight of the substance because it can vary depending on the reaction in which the substance is involved. For example, in order to determine the equivalent weight

of nitric acid in its reaction with an alkali, the molecular mass should be divided by unity: $E = M/1$ (because one singly charged hydrogen ion interacts with the hydroxyl ion in this reaction). If, however, nitric acid acts as an oxidant and reduces to NO, the nitrogen alters its degree of oxidation from +5 to +2 by the attachment of three electrons. The equivalent weight of nitric acid will thus be one third of the molecular mass:

$$E_{HNO_3} = M/3.$$

If nitric acid is reduced to ammonia in a reaction (the oxidation degree of nitrogen in ammonia is —3), the equivalent weight of HNO_3 will be equal to the molecular mass divided by 8 because $(+5) - (-3) = 8$.

As a rule the equivalent weight of H_2SO_4 is assumed to be half its molecular weight, i.e. 49.04, because sulphuric acid is dibasic. But this holds only for chemical reactions where both its singly charged hydrogen ions interact, for example, in the reaction of complete neutralization:

$$H_2SO_4 + 2KOH = K_2SO_4 + 2H_2O.$$

In the reaction

$$H_2SO_4 + KOH = KHSO_4 + H_2O$$

only one hydrogen ion is replaced in sulphuric acid molecule and the equivalent weight of sulphuric acid will be equal to its molecular mass, that is 98.08. So if we prepare an acid solution containing 980.8 g of the acid in one litre, its concentration will be $20N$ in the first and $10N$ in the second reaction. Hence, the concepts of equivalent weight of a substance and normality of a solution become meaningful only when applied to concrete chemical reactions.

Conversion of concentration units. To convert percent concentration into molar or normal concentration (and back) it is necessary to know the density of a solution, since percent concentration is the weight of solute in 100 parts by weight of solution, while molar and normal concentrations indicate the amount of solute in one litre. It follows, therefore, that in order to solve the problem of conversion, it is necessary to find the volume of a given mass, and the

mass of a given volume, by dividing the mass (or by multiplying the volume) by the density of a given solution.

Example 4. Determine the molarity of a 62 per cent solution of sulphuric acid.

Solution. Determining the molarity of solution means finding out how many moles of anhydrous H_2SO_4 are contained in one litre of its solution. The density of a 62 per cent acid solution is 1.520 g/cc (see Appendix, Table 9). Hence, one litre of sulphuric acid weighs 1520 g.
Whence:

$$\begin{matrix} 100 - 62 \\ 1520 - x \end{matrix} \qquad x = \frac{1520 \times 62}{100} = a \text{ g.}$$

To calculate the molarity:

$$M = \frac{a}{\text{mol. mass}} = \frac{1520 \times 62}{100 \times 98} = 9.6.$$

In order to convert molarity (or normality) into percent concentration, it is necessary to use tables of the densities of solutions of various molarities (or normalities). When performing approximate calculations, densities of very dilute solutions (of the order of 1 per cent) can be assumed to be unity, which gives an error of the order of 1 per cent.

Mixing and Diluting Solutions. If we dilute a solution with water, its concentration changes in inverse proportion to the change in its volume. If the volume of a solution is doubled, its concentration is halved. The same holds if several solutions are mixed: the concentrations of all solutions in the mixture decrease*.

Example 5. Mixed together are 5 ml of a $1M$ solution of substance A, 3 ml of a $2M$ solution of substance B, and 2 ml of a $4M$ solution of substance C. Determine the concentration of each solute after mixing the solutions.

Solution. The total volume of the solution after mixing is

$$5 + 3 + 2 = 10 \text{ ml.}$$

* The absolute quantities of solutes (in grams, gram-equivalents, or moles) remain unchanged after mixing or diluting solutions.

Hence the concentration of the new solution, with respect to each substance dissolved in the initial solutions, will decrease correspondingly. The volume of the first solution before mixing was 5 ml and after mixing the same amount of the solute is dissolved in 10 ml. Hence the concentration of substance A in the new solution is halved:

$$[\mathrm{A}] = \frac{1 \times 5}{10} = 0.5M.$$

The concentrations of the two other substances (B and C) change accordingly:

$$[\mathrm{B}] = \frac{2 \times 3}{10} = 0.6M \quad [\mathrm{C}] = \frac{4 \times 2}{10} = 0.8M.$$

When two solutions of the same substance but with different concentrations are mixed together, a solution with a new concentration is obtained. If we mix a% solution with b% solution of the same substance, we obtain a new solution having the concentration c%, and if $a > b$, then $a > c > b$. The new concentration is closer to the concentration of the solution with the greater initial volume. This rule can be formulated as the law of mixing: *quantities of mixed solutions are inversely proportional to the absolute differences in their concentrations and the concentration of the resultant solution.* This law can be expressed by the following mathematical formula:

$$\frac{m_A}{m_B} = \frac{c-b}{a-c}$$

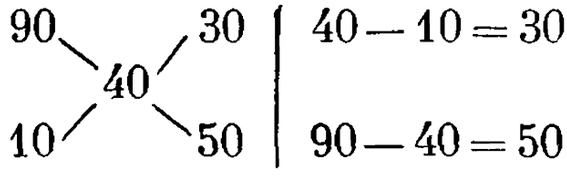
where m_A and m_B are the qu ntities of solutions A and B to be mixed and a, b, and c are the concentrations of solutions A, B, and the resultant solution. It should be remembered that if the concentrations are expressed in per cent the amounts of the initial solutions should be expressed in units of mass, and if in moles/litre or g-equiv/litre, the amounts of the initial solutions should be expressed only in litres.

If we want to calculate the ratio in which two solutions of known concentrations should be mixed to obtain a solution of a required concentration, the *cross rule* is used. The required concentration is written at the point of intersection

of two straight lines, the concentrations of the initial solutions are written beside the left-hand ends of the lines (the greater concentration beside the higher and the smaller beside the lower). The required amounts of the solutions, obtained by reading along the line and subtracting the smaller quantity from the large one, are written on the right.

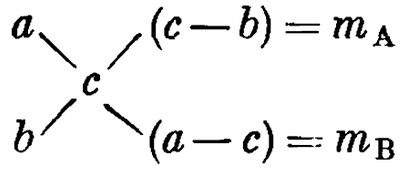
Example 6. In what ratio should a 90 per cent solution of H_2SO_4 be mixed with a 10 per cent solution of the acid to obtain a 40 per cent solution?

Solution. Using the cross rule, we find



Thus, 30 parts by weight of a 90 per cent solution of the acid should be mixed with 50 parts by weight of its 10 per cent solution.

In a generalized form, the problem is solved as follows:



If we want to calculate the quantities of solutions of known concentrations that should be mixed together in order to obtain a required quantity of a new solution with a new concentration, the ratio $m_A : m_B$ is first determined as in the previous example, and the required quantity is then divided proportionally to this ratio.

Example 7. What weights of a 90 per cent and a 10 per cent solution of sulphuric acid should be mixed to prepare 1600 g of its 40 per cent solution?

Solution. As in Example 6, the ratio $m_A : m_B = 30 : 50$ is first determined. Next, 1600 is divided into two parts according to this ratio:

$$m_A = \frac{1600 \times 30}{30+50} = 600 \text{ g}; \quad m_B = \frac{1600 \times 50}{30+50} = 1000 \text{ g}$$

i.e. 600 g of a 90 per cent solution should be mixed with 1000 g of a 10 per cent solution of the acid.

Example 8. How many grams of a 90 per cent sulphuric acid should be added to 500 g of a 10 per cent solution of the acid in order to prepare its 70 per cent solution?

Solution. Using the cross rule, we find

$$\begin{array}{ccc|l} 90 & & 60 & 70-10=60 \\ & \diagdown\ \diagup & & \\ & 70 & & \\ & \diagup\ \diagdown & & \\ 10 & & 20 & 90-70=20 \end{array}$$

Thus, 20 g of a 10 per cent solution should be mixed with 60 g of a 90 per cent solution. But the problem calls for 500 g instead of 20 g of the 10 per cent solution of the acid. Therefore, we set out the proportion:

$$\begin{array}{l} 20-60 \\ \\ 500-x \end{array} \qquad x=\frac{500\times 60}{20}=1500 \text{ g.}$$

If the problem gives the concentrations in per cent and the quantities of the solutions in volumes, the latter should be converted into weight units, by multiplying the volumes of the solutions by their densities (using the tables in the Appendix).

Example 9. What weights of 25 and 95 per cent sulphuric acid solutions should be mixed to prepare one litre of a 50 per cent solution of the acid?

Solution. Find the weight ratio in which the solutions should be mixed:

$$\begin{array}{ccc|l} 95 & & 25 & 50-25=25 \\ & \diagdown\ \diagup & & \\ & 50 & & \\ & \diagup\ \diagdown & & \\ 25 & & 45 & 95-50=45 \end{array}$$

But mixing 25 and 45 g of the starting solutions we obtain only 70 g of a 50 per cent solution, while the problem requires one litre of a 50 per cent solution weighing 1395 g (density 1.395 g/cc). To determine the quantities of the starting solutions required to prepare one litre of a 50 per cent acid, 1395 should be divided into two parts in the ratio of 25:45.

Two proportions should be set out:
for a 95 per cent solution —

25 g will give 70 g

$$x = \frac{1395 \times 25}{70} = 498 \text{ g};$$

x g will give 1395 g

for a 25 per cent solution —

45 g will give 70 g

$$y = \frac{1395 \times 45}{70} = 897 \text{ g}.$$

y g will give 1395 g

If the quantities of the starting solutions should be expressed in millilitres, the calculated weights should be divided by the densities of the original solutions:

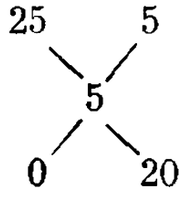
$$\frac{498}{1.834} = 271.5 \text{ ml}; \quad \frac{897}{1.178} = 761.5 \text{ ml}.$$

In practice, such calculations are approximate.

Problems in which solutions are diluted with pure solvents can be solved using the cross rule as well. In such cases, a pure solvent is assumed to be the second solution with a zero concentration.

Example 10. How much water should be added to 100 g of a 25 per cent solution of ammonia to obtain a 5 per cent solution?

Solution. Use the cross rule to determine the ratio of quantities of the starting solution and water:



$$\frac{m_{25\%\ NH_3}}{m_{water}} = \frac{5}{20}.$$

As in Example 8, determine the quantity of water required to prepare the solution:

5 — 20

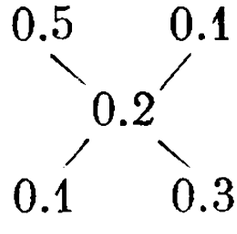
$$x = \frac{100 \times 20}{5} = 400 \text{ g}.$$

100 — x

To solve problems in which the concentrations of solutions are expressed in mole/litre or g. equiv/litre, proceed in the same way but express the quantities of the solutions in litres.

Example 11. How many millilitres of 0.5*M* and 0.1*M* solutions should be mixed to prepare 1000 ml of a 0.2*M* solution?

Solution.

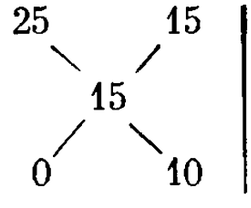


$$\frac{v_{0.5}}{v_{0.1}} = \frac{1}{3}; \qquad v_{0.5} = \frac{1000 \times 1}{4} = 250 \text{ ml}$$

$$v_{0.1} = \frac{1000 \times 3}{4} = 750 \text{ ml}.$$

Example 12. How many grams of a 25 per cent solution of KOH should be added to 400 ml of water to prepare a 15 per cent solution?

Solution. Use the cross rule to show that a 25 per cent solution and water should be mixed in the following ratio:



$\frac{15}{10}$ or $\frac{3}{2}$.

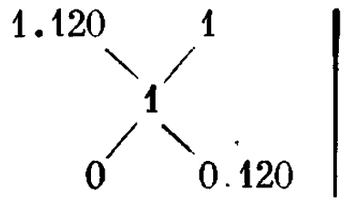
Solve the proportion:

2 g of water are required per 3 g of 25% solution
400 g of water are required per x g of 25% solution

$$x = \frac{400 \times 3}{2} = 600 \text{ g}.$$

Example 13. How many millilitres of water should be added to 1000 ml of a 1.120*N* solution of sulphuric acid to obtain an accurately 1*N* solution?

Solution. Use the cross rule to solve the following:



1—0.120

1000—x

$$x = \frac{1000 \times 0.120}{1} = 120 \text{ ml}.$$

The same result can be obtained by simple logic. One litre of solution contains 1.120 gram-equivalents of solute. If this quantity had been contained in 1120 ml, the solution would have been accurately $1N$ (because one litre would have contained one gram-equivalent). Hence, to make an accurately $1N$ solution, 120 ml of water should be added.

Example 14. How many millilitres of water and hydrochloric acid (density, 1.19 g/cc) are required to prepare 12.0 litres of $2N$ acid?

Solution. First determine the normality of the HCl solution. To that end consult the table in the Appendix first. It shows that the solution contains 38 per cent HCl and one litre weighs 1190 g.

100 g of solution contain 38 g of HCl

1190 g of solution contain x g of HCl

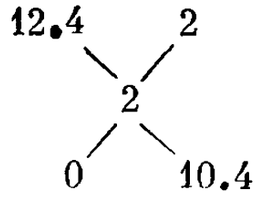
$$x = \frac{38 \times 1190}{100} = a \text{ g}.$$

Hence the normality of a 38 per cent acid solution is

$$\frac{a}{36.47} = \frac{38 \times 1190}{100 \times 36.47} = 12.4N,$$

where 36.47 is the molecular mass of HCl.

Using the cross rule determine the volumes of water and of a $12.4N$ solution of HCl that should be mixed to prepare the solution of the wanted concentration:



$$\frac{v_{HCl}}{v_{H_2O}} = \frac{2}{10.4} = \frac{1}{5.2}$$

But one litre of HCl and 5.2 litres of water will make only 6.2 litres of the acid, whereas the problem requires

that 12.0 litres of 2*N* HCl be prepared. Hence solve the proportions:

1 litre of HCl having a density of 1.19 g/cc gives 6.2 litres of 2.0*N* HCl
x litres of HCl having a density of 1.19 g/cc give 12 litres of 2.0*N* HCl
5.2 litres of water give 6.2 litres of 2.0*N* HCl
y litres of water give 12.0 litres of 2.0*N* HCl

$$x = \frac{12.0}{6.2} = 1.9 \text{ litres and } y = \frac{5.2 \times 12.0}{6.2} = 10.1 \text{ litres.}$$

While using the cross rule to solve problems in which solutions whose concentrations are expressed in moles per litre or g. equiv. per litre are mixed (or such solutions are mixed with water), it is necessary to remember that in practice accurate results are only obtained in cases where the difference between the densities of the initial and resultant solutions is insignificant. The error in calculations dealing with the mixing of about 37*N* H_2SO_4 (density, 1.836 g/cc) with large quantities of water can be as great as 5 per cent.

Problems

Percent Concentration

1. How many grams of sodium chloride are required to prepare 400 g of a 15 per cent solution?

2. How many grams of ammonium chloride are required to prepare 1.6 kg of a 10 per cent solution?

3. What is the percent concentration of a solution obtained by dissolving 7.5 g of sodium nitrate in 42.5 g of water?

4. 15 g of sodium chloride are dissolved in 100 g of water. Determine the percent concentration of the solution.

5. 8.5 g of iodine are dissolved in 100 ml of alcohol (density, 0.80 g/cc). Determine the percent concentration of the obtained solution.

6. The solubility of iodine in a 95 per cent alcohol solution is 14.8 g in 100 g. Determine the percent concentration of a saturated solution of iodine in alcohol.

7. How many grams of water will dissolve 12 g of sodium chloride to make a 5 per cent solution?

8. How many millilitres of alcohol (density, 0.80 g/cc) are required to prepare a 10 per cent solution from 5 g of iodine?

9. How many grams of table salt containing 15 per cent moisture are required to prepare 1000 g of a 20 per cent salt solution?

10. How many grams of a 60 per cent solution of potassium hydroxide and water should be used to prepare 500 g of a 10 per cent solution?

11. How many grams of commercial sodium hydroxide containing 97.00 per cent NaOH are required to prepare 1500 g of a 10.00 per cent aqueous solution?

12. How many grams of commercial sodium hydroxide containing 75 per cent Na_2O are required to prepare 600 g of a 15 per cent solution of NaOH?

13. How many grams of copper sulphate crystal hydrate are required to prepare 50 g of an 8 per cent solution?

14. If 300 g of solution contain 10 per cent anhydrous soda, how many grams of decahydrous crystal hydrate of sodium carbonate are required to prepare this solution?

15. Prepared are 250 g of a 3.0 per cent solution of borax. How many grams of decahydrous sodium tetraborate and water are required?

16. How many grams of water are required to prepare a 10 per cent solution of barium chloride from 35 g of its dihydrate?

17. How many grams of anhydrous sulphuric acid are contained in 20.00 ml of a 50.00 per cent solution?

18. How many grams of HCl, HNO_3, and H_2SO_4 are contained in 1 ml of concentrated hydrochloric (density, 1.19 g/cc), nitric (density, 1.40 g/cc), and sulphuric (density, 1.836 g/cc) acids?

19. One volume of water at 20°C dissolves 0.878 volume of CO_2 (at STP)*. Determine the percent concentration of a saturated at 20°C solution of this gas in water.

20. One volume of water at 20°C dissolves 702 volumes of ammonia at STP. What is the percent concentration of a saturated at 20°C solution of ammonia in water?

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* Standard temperature and pressure.

21. One volume of water at 20°C dissolves 2.58 volumes of hydrogen sulphide at STP. What is the percent concentration of a saturated at 20°C solution of the gas in water?

22. If 100 g of water at 20°C dissolve 11.3 g of SO_2, determine the percent concentration of the resultant solution.

23. If 60 g of water dissolve 10 g of potassium chloride, determine the percent concentration of the resultant solution.

24. If 3 g of potassium iodide are dissolved in 30 g of water, determine the percent concentration of the solution obtained.

25. If 10.0 g of $BaCl_2 \cdot 2H_2O$ are dissolved in 90 g of water, calculate the percent concentration of $BaCl_2$ in the solution.

26. If 5.0 g of sodium nitrate are dissolved in 50 g of water, determine the percent concentration of solution obtained.

27. If 20 ml of a 40 per cent phosphoric acid (density, 1.254 g/cc) are dissolved in 60 g of water, determine the percent concentration of the solution obtained.

28. If 3 litres of water are added to 1000 g of an 80 per cent acetic acid, determine the percent concentration of the solution obtained.

Molar and Normal Concentrations

29. Determine the equivalent weight of sulphuric acid in the following reactions: (a) complete neutralization; (b) incomplete neutralization; (c) reduction to free sulphur; to hydrogen sulphide.

30. What is the equivalent weight of nitric acid in the following reactions: (a) neutralization; (b) reduction to NO_2, to NO, and to ammonia?

31. Calculate the equivalent weight of hydrogen sulphide in the following reactions: (a) neutralization; (b) oxidation to free sulphur, to SO_2, and to sulphuric acid.

32. Calculate the equivalent weight of SO_2 in the following reactions: (a) with two molecules of alkali; (b) oxidation to sulphuric acid; (c) reduction to free sulphur.

33. Determine the gram-equivalent of potassium permanganate in the following reactions: (a) exchange reaction; (b) reduction to manganate, to MnO_2, and to Mn^{2+}.

34. Determine the equivalent weight of potassium chromate in the following reactions: (a) exchange reaction; (b) reduction to Cr^{3+}.

35. Determine the gram-equivalent of ferric-ammonium sulphate, $NH_4Fe\,(SO_4)_2 \cdot 12H_2O$, in the following: (a) reaction for ammonium ion; (b) reaction for iron ion; (c) reaction for sulphate ion.

36. Determine the gram-equivalent of ferric chloride in the following reactions: (a) exchange reaction; (b) reduction to Fe^{2+}.

37. Determine the gram-equivalent of potassium dichromate in the reactions of (a) exchange and (b) reduction to Cr^{3+}.

38. Determine the gram-equivalent of ferrous sulphate, $FeSO_4 \cdot 7H_2O$, in the following reactions: (a) exchange reaction; (b) oxidation to Fe^{3+}.

39. Determine the equivalent weight of Mohr's salt, $(NH_4)_2Fe\,(SO_4)_2 \cdot 6H_2O$, in the following: (a) reaction for NH_4^+ ion; (b) reaction for Fe^{2+} ion; (c) oxidation of iron to Fe^{3+}.

40. By what number should the molecular masses of Na_2O, Fe_2O_3, $Ba(OH)_2$, and $Ca_3(PO_4)_2$ be divided to determine their equivalent weights in reactions with sulphuric acid, provided neutral salts are obtained in all cases?

41. Determine the equivalent weight of oxalic acid, $H_2C_2O_4 \cdot 2H_2O$, in the following reactions: (a) exchange reaction; (b) oxidation with potassium permanganate to CO_2.

42. Determine the gram-equivalent of stannous chloride in the following reactions: (a) exchange reaction; (b) oxidation.

43. If 250.0 ml of sulphuric acid solution contain 1.226 g of the monohydrate, determine the molarity and normality (to complete neutralization) of the solution.

44. If 600.0 ml of solution contain 11.76 g of orthophosphoric acid, determine its (a) molarity and (b) normality for complete and incomplete (first and second step of dissociation) neutralization of the solution.

45. If 20 mg of $CuSO_4$ are contained in 1 ml of solution,

determine the molarity and normality of the solution (for exchange reactions).

46. 10.600 g of anhydrous sodium carbonate are dissolved in water in a 500-ml flask, and water is added to the mark. Determine the molarity and normality (for complete and incomplete neutralization) of the solution.

47. Determine the molarity and normality of (a) sulphuric; (b) hydrochloric; and (c) nitric acids having the same density of 1.14 g/cc.

48. Determine the normality (for complete neutralization) of the following acids: (a) sulphuric (density, 1.836 g/cc); (b) nitric (density, 1.400 g/cc); and (c) hydrochloric (density, 1.189 g/cc).

49. Determine the normality (for a neutralization reaction) of a solution having a density of 0.910 g/cc and containing 24 per cent by mass of NH_3.

50. Determine the molarity and normality (for complete and incomplete neutralization) of a solution containing 18 per cent of H_3PO_4 (density, 1.100 g/cc).

51. How many grams of sulphuric acid are contained in 1 ml of a 0.1000*N* solution?

Note: Unless stated otherwise, normality will further refer to exchange reactions or to reactions of complete neutralization, or else to a reaction specific for a given substance (e.g. the reaction of oxidation of a substance in an acid medium with reduction of Mn^{7+} to Mn^{2+} is specific for $KMnO_4$).

52. How many grams of hydrogen chloride are contained in 200 ml of a 0.005*N* solution of HCl?

53. How many grams of copper sulphate will crystallize from 5 ml of a 0.200*N* solution?

54. How many grams of sodium carbonate will crystallize from one drop (0.05 ml) of a 0.100*N* solution of the crystal hydrate?

55. How many milligrams of the Na^+ ion are contained in 10.00 ml of a 0.2000*N* solution of NaCl?

56. How many milligrams of the Cl^- ion are contained in 1.00 ml of a 0.500*N* solution of HCl?

57. Calculate the percent concentration of ammonia in a 15*N* solution of NH_4OH (density, 0.898 g/cc).

58. What is the percent concentration of a 6*N* solution of HCl (density, 1.098 g/cc)?

59. Determine the percent concentration of a 6*N* solution of the following acids: (a) sulphuric (density, 1.18 g/cc); (b) nitric (density, 1.19 g/cc); (c) acetic (density, 1.043 g/cc).

60. Determine the percent concentration and molarity of 1.9*N* H_3PO_4 (density, 1.031 g/cc).

61. How many grams of pure sodium hydroxide are required to prepare 500 ml of a 0.10*N* solution?

62. How many grams of pure anhydrous soda are required to prepare 500 ml of a 0.100*N* solution?

63. How many grams of pure borax are required to prepare 250 ml of a 0.050*N* solution?

64. How many grams of glacial acetic acid are required to prepare 2 litres of a 2*N* solution?

65. How many litres of hydrogen chloride (at STP) should be dissolved to prepare 10.00 litres of a 0.100*N* solution?

66. How many millilitres of CO_2 (at STP) should be dissolved to prepare 500 ml of a 0.0500*N* solution of H_2CO_3?

67. Determine the molarity and normality of a saturated at 20°C solution of hydrogen sulphide in water obtaining the necessary data from the tables in the Appendix and assuming the density of the solution to be about unity.

68. Determine the molarity and normality of sulphurous acid obtained by the saturation of water at 20°C with SO_2 obtaining the necessary data from the tables and assuming the density of the solution to be about unity.

69. How many grams of 36 per cent hydrochloric acid are required to prepare 5 litres of a 0.2*N* solution?

70. How many grams of sulphuric acid (density, 1.611 g/cc) are required to prepare 8.00 litres of a 0.300*N* solution?

71. How many grams of nitric acid (density, 1.40 g/cc) are required to prepare 3000 ml of a 2.000*N* solution?

72. How many grams of a 80 per cent solution of CH_3COOH are required to prepare 1500 ml of a 0.0500*N* solution of the acid?

73. How many millilitres of nitric acid (density, 1.31 g/cc) are required to prepare 3 litres of a 0.5*N* solution?

74. How many millilitres of hydrochloric acid (density, 1.198 g/cc) are required to prepare 5 litres of a 0.3*N* solution?

75. How many millilitres of a 96 per cent solution of sulphuric acid are required to prepare 6 litres of a $2N$ solution?

76. How many millilitres of a 24 per cent solution of ammonia are required to prepare 2 litres of a $0.5N$ solution?

77. How many millilitres of $2N$ HNO_3 can be prepared from 10 ml of concentrated acid (density, 1.430 g/cc)?

78. How many millilitres of $0.1N$ H_3PO_4 can be prepared from 1 ml of a solution with a density of 1.140 g/cc?

79. How many litres of $2N$ NH_4OH can be prepared from 1 litre of a 24 per cent ammonia solution?

80. How many litres of a $2N$ solution of sulphuric acid can be prepared from 100 ml of a 96 per cent solution?

81. How many millilitres of a $0.1N$ solution of sulphuric acid can be prepared from 1 ml of oleum containing 85.30 per cent of tolal SO_3 and having a density of 1.897 g/cc?

82. How many millilitres of $0.5N$ sulphuric acid can be prepared from 10.00 ml of oleum containing 30 per cent of free SO_3 and having a density of 1.931 g/cc?

83. How many grams of potassium aluminium sulphate, $KAl(SO_4)_2 \cdot 12H_2O$, are required to prepare 3 litres of a $0.5N$ solution, if it is to be used to identify in it the following ions: (a) K^+; (b) Al^{3+}; (c) SO_4^{2-}?

84. How many grams of Mohr's salt are required to prepare 2 litres of a $0.5N$ solution, if it is intended to identify in it the following ions: (a) NH_4^+; (b) Fe^{2+}; (c) SO_4^{2-}?

85. How many grams of $KMnO_4$ are required to prepare 5 litres of a 0.1 N solution, if it is intended to be used in (a) an exchange reaction; (b) reduction to MnO_2; (c) reduction to Mn^{2+}?

86. How many grams of potassium dichromate are required to prepare 2.5 litres of a $0.2N$ solution if it is intended for (a) a reaction with $AgNO_3$; (b) reduction to Cr^{3+}?

87. One litre of solution contains 24.11 g of ferric-ammonium sulphate. What is its normality if it is intended (a) to detect NH_4^+, Fe^{3+}, and SO_4^{2-} ions in it; (b) to reduce to Fe^{2+}?

88. If 200 ml of solution contain 25.21 g of nitric acid, what is its normality for (a) exchange reactions; (b) reduction to NO; (c) reduction to NH_3?

Note: The solubility of all substances in the problems is given in grams per 100 g of solvent (water) at 20°C.

89. Determine the solubility of calcium sulphate in mole/litre if its solubility is 0.200.

90. Determine the solubility of barium sulphate in mole/litre if its solubility is 2.3×10^{-4}.

91. Determine the molarity of a saturated silver chloride solution if its solubility is 1.5×10^{-4}.

92. Determine the molarity of a saturated magnesium hydroxide solution if its solubility is 0.9×10^{-3}.

93. Determine the molarity of saturated aqueous solutions of lead chloride, barium carbonate, strontium sulphate, and silver bromide using the tables.

94. Determine the molarity of saturated aqueous solutions of silver thiocyanate, carbonate, and iodide.

Mixing and Diluting Solutions

95. Mixed are equal volumes of a 0.5*N* solution of potassium chloride and a 0.2*N* solution of sodium nitrate. Determine the concentration of each solute in the resultant solution.

96. Mixed are equal volumes of a 1*N* solution of zinc sulphate, a 0.5*N* solution of magnesium chloride, and a 0.3*N* solution of potassium nitrate. Determine the concentration of each solute in the resultant solution.

97. Mixed are 50 ml of a 0.5*M* solution of barium chloride with 10 ml of a 0.5*M* solution of magnesium nitrate. Determine the concentration of each solute in the resultant solution.

98. Mixed are 20 ml of a 0.3*M* solution of sodium bromide with 5 ml of a 0.8*M* solution of sodium chloride. Determine the concentration of each solute in the resultant solution.

99. Mixed are equal volumes of a saturated solution of calcium sulphate (0.2 g/100 g of H_2O) and 0.1*M* solution of strontium nitrate. Determine the concentration, in gram-ion/litre, of the strontium ion and sulphate ion in the solution at the moment of mixing.

100. Mixed are 10 ml of a saturated solution of lead chloride and 20 ml of gypsum water. Determine the concentra-

tion, in gram-ion/litre, of the lead ion and sulphate ion at the moment of mixing.

101. In what weight ratio should 38 per cent hydrochloric acid be mixed with 10 per cent hydrochloric acid to prepare a 15 per cent solution?

102. In what weight ratio should a 24 per cent ammonia solution be mixed with a 5 per cent solution to obtain a 10 per cent solution of ammonia?

103. In what weight ratio should an 80 per cent solution of sulphuric acid be mixed with a 20 per cent acid to obtain a 60 per cent solution?

104. In what weight ratio should a 15 per cent solution of acetic acid be mixed with a 3 per cent solution of the acid to prepare a 10 per cent solution?

105. How many grams of a 96 per cent and a 20 per cent solution of sulphuric acid should be used to prepare 1000 g of a 40 per cent solution?

106. How many grams of a 5 and an 80 per cent solution of nitric acid should be used to prepare 2 kg of a 20 per cent solution?

107. How many grams of a 90 and a 25 per cent solution of sulphuric acid should be used to prepare 1000 g of a 40 per cent solution?

108. How many kilograms of a 5 and a 25 per cent solution of ammonia should be used to prepare 4 kg of a 20 per cent solution of ammonia?

109. How many grams of a 5 per cent salt solution should be added to 500 g of a 40 per cent solution to prepare a 20 per cent solution?

110. How can a 20 per cent solution of nitric acid be prepared from 100 g of a 50 per cent solution and a 10 per cent solution of the acid?

111. How many millilitres of a 5 and a 30 per cent solution of potassium hydroxide should be used to prepare 600 ml of a 10 per cent solution?

112. How many millilitres of a 10 and a 90 per cent solution of nitric acid should be used to prepare 1500 ml of a 16 per cent solution?

113. In what weight ratio should a 62 per cent solution of sulphuric acid and water be mixed to prepare a 12 per cent solution of the acid?

114. In what weight ratio should a 50 per cent solution of sodium hydroxide and water be mixed to prepare a 30 per cent solution of the alkali?

115. How many grams of water and a 36 per cent solution of hydrochloric acid should be used to prepare 1000 g of a 20 per cent solution of the acid?

116. How many kilograms of water and a 25 per cent solution of ammonia should be used to prepare 5 kg of a 10 per cent solution?

117. How many grams of water should be added to 200 g of a 20 per cent solution of hydrochloric acid to prepare a 5 per cent solution?

118. How many grams of a 96 per cent solution of sulphuric acid should be added to 1.00 litre of water to prepare a 10 per cent solution of the acid?

119. How many litres of water should be added to 1 kg of a 10 per cent solution of ammonia to prepare a 2.5 per cent solution?

120. How many grams of a 50 per cent solution of acetic acid should be added to 250 ml of water to obtain a 12 per cent solution of the acid?

121. How many millilitres of water should be added to 100 ml of a 24 per cent solution of ammonia to prepare a 5 per cent solution?

122. How many millilitres of water should be added to 1.00 litre of hydrochloric acid (density, 1.189 g/cc) to prepare a 18 per cent solution?

123. How many millilitres of water and a 60 per cent solution of sulphuric acid should be used to prepare 1.00 litre of a 10 per cent solution?

124. How can 10 kg of a 20 per cent solution of nitric acid be prepared from a 67 per cent solution?

125. How can 200 ml of a 30 per cent solution of sulphuric acid be prepared from a 96 per cent solution?

126. How many millilitres of water and a 24 per cent solution of ammonia should be used to prepare 1.00 litre of a 10 per cent solution?

127. How many millilitres of water and a 80 per cent solution of acetic acid should be used to prepare 5.00 litres of a 3 per cent solution?

128. Determine the percentage of ammonia in the solu-

tion obtained by diluting 1.00 litre of a 28 per cent solution with 9.00 litres of water.

129. Add 40 ml of water to 10 ml of a 20 per cent solution of hydrochloric acid. What is the percent concentration of the resultant solution?

130. How many millilitres of a 50 and a 20 per cent solution of sodium hydroxide should be used to prepare 500 ml of a 40 per cent solution?

131. In what weight ratio should a $12N$ solution of HCl and a $2N$ solution of the same acid be mixed to prepare a $4N$ solution?

132. In what volume ratio should $6N$ HNO_3 and water be mixed to prepare a $2N$ solution of the acid?

133. In what volume ratio should a $1N$ solution of acetic acid and water be mixed to prepare a $0.05N$ solution of the acid?

134. In what volume ratio should a $0.5N$ and a $0.1N$ solution of sodium hydroxide be mixed to prepare a $0.2N$ solution?

135. How many millilitres of a $6N$ and a $1N$ solution of nitric acid should be mixed to prepare 500 ml of a $2N$ solution?

136. How many millilitres of a $2N$ and a $0.2N$ solution of potassium hydroxide are required to prepare 1.8 litres of a $0.6N$ solution?

137. How many millilitres of a $0.1N$ solution of nitric acid should be added to 200 ml of a $0.5N$ solution to prepare a $0.2N$ solution of the acid?

138. How many millilitres of a $6N$ solution of hydrochloric acid should be added to 250 ml of a $0.3N$ solution of the acid to obtain a $0.5N$ solution?

139. How many millilitres of water should be added to 1.00 litre of a $0.125N$ solution of sodium hydroxide to obtain a $0.1000N$ solution?

140. How many millilitres of water should be added to 10.0 ml of a $12N$ solution of hydrochloric acid to obtain a $0.1N$ solution?

141. How many litres of water and a $13N$ solution of NH_4OH should be used to prepare 3 litres of a $4N$ solution of ammonium hydroxide?

142. How many litres of water and $2N$ sulphuric acid should be taken to prepare 5 litres of a $0.05N$ solution?

143. How many millilitres of water and $12N$ sulphuric acid should be taken to prepare 500 ml of a 20 per cent solution of the acid?

144. How many millilitres of water should be added to 1500 ml of a $13N$ solution of NH_4OH to prepare a 14 per cent solution?

145. A $0.100N$ solution of NaCl is prepared in a 250-ml volumetric flask, and its 25.00 ml withdrawn by a pipette. How many grams of NaCl should be added to the flask so that the normality of the solution, after adding water to the mark, is $0.2500N$?

146. A $0.2500N$ solution of KCl is prepared in a 200-ml volumetric flask, and its 50.00 ml withdrawn by a pipette. What quantity, in grams, of pure KCl should be added to the flask so that, after adding water to the mark, the normality of the solution is $0.5000N$?

147. A $0.1822N$ solution of Na_2CO_3 is prepared in a 500-ml volumetric flask, its 50.00 ml are withdrawn. Next 8.0540 g of the same anhydrous reagent and water are added to the mark. Determine the normality of the resultant solution.

148. Using a pipette, 50.00 ml of a $0.0520N$ solution of $Na_2B_4O_7$ (Eq. wt. $_{Na_2B_4O_7} = M : 2$) are taken from a 250-ml volumetric flask and 2.2784 g of $N_2B_4O_7 \cdot 10H_2O$ are added. The salt and water are added to the mark. Determine the normality of the solution obtained.

149. A $0.1200N$ solution of sulphuric acid is prepared in a 500-ml volumetric flask, its 25.00 ml are withdrawn and 3.4740 g of H_2SO_4 (density, 1.836 g/cc) added. What is the normality of the solution obtained after adding water to the mark?

150. A $0.09650N$ solution of sulphuric acid is prepared in a 250-ml volumetric flask, and its 25.00 ml withdrawn. How many grams of H_2SO_4 (density, 1.611 g/cc) should be added to the flask so that the normality of the solution, after adding water to the mark, is $0.2000N$?

B. Chemical equilibrium

The rate of a chemical reaction is measured by the quantity of moles of the reaction product formed per unit time. The rate of a chemical reaction depends on the reaction conditions, but the analyst can usually vary the reaction rate by altering the concentrations of the reactants. The relationship between the rate of a chemical reaction and the concentration of the reactants is described by the law of mass action which reads: *the rate of a chemical reaction is proportional to the product of concentrations of the reactants.* This law was formulated by Guldberg and Waage (1864). If m moles of substance A and n moles of substance B take part in the reaction, the rate of the reaction v will be

$$v = k[A]^m[B]^n$$

where [A] and [B] are concentrations of substances A and B, in moles/litre, and k is the proportionality factor.

The law is sufficiently accurate only for reactions in homogeneous media, e.g. between gases or solutions. For reactions occurring in heterogeneous media the rate of reaction can be assumed to be approximately proportional only to the concentration of that substance which is present in a dissolved or gaseous state.

Example 1. Write down the expression of the law of mass action for the following reactions:

$$\text{(a) } H_2 + Br_2 = 2HBr$$

$$\text{(b) } Na_2S_2O_3 + 2HCl = 2NaCl + SO_2 + S + H_2O$$

$$\text{(c) } C + O_2 = CO_2$$

Solution.

$$\text{(a) } v = k\,[H_2]\,[Br_2]$$

$$\text{(b) } v = k\,[Na_2S_2O_3]\,[HCl]^2$$

$$\text{(c) } v = k\,[O_2]$$

If in any particular case the concentration of each reactant is equal to 1 mole/litre, then $v = k$. This explains the chemical sense of the proportionality factor in the expression of the law of mass action: it equals the rate of the reaction

provided the concentration of each reactant equals 1 mole/litre. The quantity k is also known as the *velocity constant* of a chemical reaction.

The law of mass action predicts the change in the reaction rate with varying concentrations of all or some of the reactants.

Example 2. How will the rate of the reaction between hydrogen and bromine change if their concentrations are doubled?

Solution. Write down the expression of the law of mass action for this particular case:

$$v = k[H_2][Br_2].$$

Let the initial concentrations of hydrogen and bromine be $[H_2] = a$ moles and $[Br_2] = b$ moles. Then

$$v = kab.$$

The increased concentrations will then be

$$v_1 = k2a2b = 4kab$$

i.e. after doubling the concentration of each reactant, the rate of the reaction quadruples.

Example 3. The initial concentrations of the reactants in the reaction

$$Na_2S_2O_3 + 2HCl = 2NaCl + S + SO_2 + H_2O$$

were (in moles/litre): $[Na_2S_2O_3] = 1$ and $[HCl] = 2$. How will the rate of the reaction change if the concentration of sodium thiosulphate remains unchanged while the concentration of the acid increases to 6 moles/litre?

Solution. According to the law of mass action the initial reaction rate (before changing the concentration of HCl) is

$$v = k[Na_2S_2O_3][HCl]^2 = k \times 1 \times 2^2 = k \cdot 4.$$

After increasing the concentration the reaction rate is

$$v_1 = k \times 1 \times 6^2 = k \cdot 36.$$

The reaction rate increases nine times.

Example 4. How will the reaction rate in the previous example change if the concentration of sodium thiosulphate also increases to 3 moles/litre?

Solution.

$$v_2 = k \times 3 \times 6^2 = k \cdot 108.$$

The reaction rate will increase 27 times.

Variations in reaction rates with changing concentrations of the reactants can also be determined in the general form, .e. without specifying the concentrations.

Example 5. How will the reaction rate change in

$$A + 2B \rightleftharpoons 2D + E$$

if the concentration of substance A increases two and of substance B four times?

Solution. Let us designate the velocity constant by k, the concentration of substance A by x, the concentration of substance B by y, the initial reaction rate by v_1, and the rate after changing the concentrations by v_2. Then

$$v_1 = kxy^2, \; v_2 = k2x\,(4y)^2 = k2x \times 16y^2.$$

Divide v_2 by v_1:

$$\frac{v_2}{v_1} = \frac{k2x \times 16y^2}{kxy^2} = 32.$$

The reaction rate increases 32 times.

It should be remembered that when using the law of mass action the concentrations of the reactants in the solution after mixing should be substituted into the formula, not the initial concentrations. (See Example 5 in Section A.)

In the course of a chemical reaction, the concentrations of the reactants decrease and the reaction rate decreases accordingly (in compliance with the law of mass action). If we could completely remove the reaction products from the mixture the reaction rate would then obey Berthollet's rule and tend to zero, i.e. the reaction would have been completed and all the original substances would have been converted into the end products. But in practice this does not occur and the reaction products accumulate in the vessel

and start interacting to form the initial substances. Thus, along with the forward reaction there also occurs a reverse reaction, until eventually a state known as *chemical equilibrium* is attained. Such chemical processes are called reversible, and the reaction can be expressed by the following equation:

$$mA + nB \rightleftharpoons pD + qE$$

where A and B are the starting substances, D and E are the reaction products, and m, n, p, and q are coefficients.

Chemical equilibrium is characterized by the invariable concentration of all reactants, equality of the forward and reverse reaction rates, and by the apparent stability of the system. The law of chemical equilibrium is derived as a direct consequence of the law of mass action: *in a state of equilibrium, the ratio of the product of the concentrations of the resultants to the product of the concentrations of the initial reactants is a constant, known as the equilibrium constant*:

$$\frac{[D]^p[E]^q}{[A]^m[B]^n} = K.$$

This law can be used to determine concentrations of the reaction products in a system at equilibrium, provided K and the concentrations of the starting reactants are known.

Example 6. After a state of equilibrium has been attained in the reaction $A + B \rightleftharpoons D + E$, the concentrations of the reactants are as follows (in moles/litre): [A] = 0.25, [B] = = 0.25, [D] = 0.75, and [E] = 0.75. Determine K.

Solution. Substitute the concentrations in the equation for the chemical equilibrium and calculate:

$$K = \frac{0.75 \times 0.75}{0.25 \times 0.25} = 9.$$

Example 7. The equilibrium constant of the reaction $A + B \rightleftharpoons D + E$ is 9. Determine the concentrations of the reaction products D and E in the system after equilibrium has been attained, when the concentrations of the starting reactants are as follows (in moles/litre): [A] = 1, [B] = 1.

Solution. Write out the reaction equation. Place the starting concentrations at the top and the concentrations

at equilibrium at the bottom of the letters designating the starting reactants and the reaction products, using x to denote the unknown concentrations:

$$\begin{array}{ccccccc} 1 & & 1 & & 0 & & 0 \\ A & + & B & \rightleftharpoons & D & + & E \\ (1-x) & & (1-x) & & x & & x \end{array}$$

Substitute the concentrations in the equation of the law of chemical equilibrium:

$$\frac{x^2}{(1-x)(1-x)} = 9.$$

whence

$$8x^2 - 18x + 9 = 0.$$

We obtain two values of the concentration: $x_1 = 1.5$ and $x_2 = 0.75$. Since the concentrations of the starting reactants A and B are 1 mole/litre, the concentrations of the resultants D and E cannot exceed 1 mole/litre. Hence x_1 does not satisfy the condition of the problem and the true answer is x_2.

Example 8. If 1 litre of a $2M$ solution of substance A and 1 litre of a $4M$ solution of substance B take part in the reaction $A + B \rightleftharpoons D + E$, determine the concentrations of substances D and E at equilibrium, given $K = 9$.

Solution. First determine the concentrations of substances A and B after mixing the solutions (see Example 5, Section A):

$$[A] = \frac{2 \times 1}{2} = 1 \text{ mole/litre}, \quad [B] = \frac{4 \times 1}{2} = 2 \text{ moles/litre}.$$

Write the reaction equation with the initial and final concentrations of all the reactants:

$$\begin{array}{ccccccc} 1 & & 2 & & 0 & & 0 \\ A & + & B & \rightleftharpoons & D & + & E \\ (1-x) & & (2-x) & & x & & x \end{array}$$

Substitute the concentrations in the equation of the law of chemical equilibrium:

$$\frac{x^2}{(1-x)(2-x)} = 9$$

whence

$$8x^2 - 27x + 18 = 0.$$

Solve the quadratic equation to obtain $x_1 = 2.46$ and $x_2 = 0.91$. Since the concentrations of the starting substances are only 1 mole/litre, the concentration of any reaction product cannot be more than 1 mole/litre. Therefore x_1 cannot be the correct answer and the true answer is x_2.

When we compare the results of Examples 7 and 8 we see that by increasing the concentration of only one starting substance we increase the concentration of the reaction products. The yield of the reaction is said to increase. *The ratio of the quantity of the resultant product obtained in a given reaction to the quantity of product that might have been obtained had the reaction continued to the end is known as the yield of the reaction.* As a rule the yield is expressed in per cent. The above examples show that a two-fold increase in the concentration of either reactant increases the yield from 75 to 91 per cent.

Example 9. The concentrations of the starting reactants A and B in the reaction $A + B \rightleftharpoons D + E$ are 2 and 3 moles/litre respectively. Determine the yield of the product E, given $K = 9$.

Solution.

2	3	0	0
A +	B	$\rightleftharpoons$ D +	E
$(2-x)$	$(3-x)$	x	x

whence, by the law of chemical equilibrium,

$$\frac{x^2}{(2-x)(3-x)} = 9; \quad 8x^2 - 45x + 54 = 0.$$

Solve the equation to obtain $x_1 = 3.89$ and $x_2 = 1.74$. In our case x cannot exceed 2, and x_2 is therefore the correct answer. The yield of the reaction is

$$\frac{100 \times 1.74}{2} = 87\%.$$

Problems

1. Write down the mathematical expressions of the rate of the following reactions:

(a) $2NO + O_2 \rightleftarrows 2NO_2$

(b) $Fe_2O_3 + 3H_2 \rightleftarrows 2Fe + 3H_2O$

2. Write down the mathematical expression of the rate of the following reactions:

(a) $CO + Cl_2 \rightleftharpoons COCl_2$

(b) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

(c) $NaCl + H_2SO_4 \rightleftharpoons NaHSO_4 + HCl$

3. The concentrations of substances A and B in the reaction

$$A + B \rightleftarrows D + E$$

are 1 mole/litre each. How will the rate of the forward reaction change if [A] remains unchanged and [B] increases to 2 moles/litre?

4. How will the rate of the forward reaction

$$C_2H_5OH + CH_3COOH \rightleftarrows CH_3COOC_2H_5 + H_2O$$

change if the concentration of ethyl alcohol increases three times and that of acetic acid decreases two times?

5. How will the rate of the forward reaction $A + B \rightleftharpoons D$ change if the concentrations of substances A and B increase three times?

6. How will the rate of the forward reaction

$$3CH_3OH + H_3BO_3 \rightleftarrows B(OCH_3)_3 + 3H_2O$$

change if the concentration of methyl alcohol changes from

0.3 to 0.6 mole/litre and the concentration of boric acid from 0.2 to 1.2 moles/litre?

7. How will the rate of the reaction

$$2A+B \rightleftharpoons 2D+E$$

change if [A] is halved and [B] is doubled?

8. How will the rate of the reaction

$$2A+B \rightleftharpoons 2D+E$$

change if [A] doubles and [B] is halved?

9. After attaining equilibrium in the reaction

$$A+B \rightleftharpoons D+E$$

[A] increases two times and [D] increases four times. In what direction will the equilibrium be shifted?

10. In what direction will the equilibrium in the reaction

$$FeCl_3+3KSCN \rightleftharpoons Fe(SCN)_3+3KCl$$

be shifted if the concentration of ferric chloride increases from 0.1 to 0.3 mole/litre and of potassium chloride from 0.4 to 1.2 moles/litre?

11. The gas pressure in the equilibrium system

$$A_2+B_2 \rightleftharpoons 2AB$$

increases (a) two times, (b) four times. How will this affect the equilibrium?

12. In what direction will the equilibrium in the system

$$3H_2+N_2 \rightleftharpoons 2NH_3$$

be shifted if the pressure in the closed vessel increases three times?

13. Equilibrium is attained in the reaction

$$C_2H_5OH+CH_3COOH \rightleftharpoons CH_3COOC_2H_5+H_2O$$

when the concentrations of the reactants, under certain conditions, are as follows in moles/litre: $[C_2H_5OH] = 0.25$, $[CH_3COOH] = 0.25$, $[CH_3COOC_2H_5] = 0.75$, and $[H_2O] = 0.75$. Determine the equilibrium constant.

14. The starting concentrations of sodium chloride and sulphuric acid in the reaction

$$NaCl + H_2SO_4 \rightleftharpoons NaHSO_4 + HCl$$

are 1 and 2.5 moles/litre, respectively. After equilibrium has been attained, the concentration of hydrogen chloride decreases to 0.75 mole/litre. What is the equilibrium constant?

15. The initial concentrations of substances A and B in the reaction

$$3A + B \rightleftharpoons 2D + E$$

are 1.5 and 2 moles/litre respectively. After equilibrium has been attained, [A] changes to 20 per cent of the initial. Determine the equilibrium constant.

16. The concentrations of methyl alcohol and sulphuric acid in the reaction

$$2CH_3OH + H_2SO_4 \rightleftharpoons (CH_3)_2SO_4 + 2H_2O$$

are 2 moles/litre and 1 mole/litre respectively. After equilibrium has been attained, the concentration of dimethyl sulphate becomes 30 per cent of the initial concentration of methyl alcohol. Determine K.

17. The equilibrium constant of the reaction

$$A + B \rightleftharpoons D + E$$

is 4. Which velocity constant, that of the forward or backward reaction, is greater? By how much is one greater than the other?

18. The equilibrium constant of the reaction

$$A + B \rightleftharpoons D + E$$

is 0.8. How do the velocity constants of the forward and the backward reactions relate?

19. Equilibrium is achieved in the reaction

$$CO + Cl_2 \rightleftharpoons COCl_2$$

when the concentrations of CO, Cl_2, and $COCl_2$ are 0.55, 0.05, and 0.95 mole/litre respectively. Determine the initial concentrations of CO and chlorine.

20. Equilibrium in the reaction

$$A + B \rightleftharpoons 2D$$

is attained when the concentrations of A, B and D are 0.35, 0.15, and 1.2 moles/litre respectively. What were the initial concentrations of A and B?

21. The equilibrium constant in the reaction

$$C_2H_5OH + CH_3COOH \rightleftharpoons C_2H_5COOCH_3 + H_2O$$

under certain conditions is 4. What is the concentration of acetic acid at the state of equilibrium, if the initial concentration of ethyl alcohol is 2 and of acetic acid 2.8 moles/litre?

22. The initial concentrations of A and B in the reaction

$$A + B \rightleftharpoons D + E$$

are 0.5 and 0.3 mole/litre respectively. What quantity, in per cent, of substance A remains unreacted if the equilibrium constant of the reaction is 1.2?

23. How will the concentration of substance D in the reaction

$$A + B \rightleftharpoons D + E$$

change if $K = 4$ and if, with a constant concentration of substance A, the concentration of substance B changes subsequently from 1 to 2, to 3 moles/litre, etc. until the reaction becomes essentially irreversible? Show graphically the relationships between [B] and [D]. Calculate to an accuracy of 0.01.

24. The equilibrium constant in the reaction

$$KCl + H_2SO_4 \rightleftharpoons KHSO_4 + HCl$$

under certain conditions is 9. How will the yield of the reaction change if, at constant [KCl] (2 moles/litre), the concentration of sulphuric acid is subsequently 1, 2, 3 moles/litre, etc., until a further increase in the concentration of the acid becomes economically inefficient (one mole of hydrogen chloride is 10 times more expensive than one mole of sulphuric acid)?

25. If 1 litre of a $2M$ solution of substance A and 2 litres of a $4M$ solution of substance B are mixed in the reaction

$$A + B \rightleftharpoons D + E,$$

how will the rate of the forward reaction change if 3 litres of the solution of substance B is used for the reaction?

26. The equilibrium constant of the reaction

$$A + B \rightleftharpoons D + E$$

is 4. Determine the yield of product D if the starting reactants were used in the following quantities: 3 litres of a $4M$ solution of substance A and 7 litres of a $2M$ solution of substance B.

27. The equilibrium constant of the reaction

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

at 850°C is unity. At what concentrations of all substances will equilibrium be attained in the system if the initial concentrations of CO_2 and H_2 are 0.1 and 0.2 mole/litre respectively?

28. What quantity, in moles/litre, of CO will be obtained in the reaction described in the previous problem, if the initial concentrations of CO_2 and H_2 are 1 and 3 moles/litre respectively?

29. The equilibrium constant in the reaction

$$A + B \rightleftharpoons D + E$$

where the reactants are 2 litres of a $3M$ solution of substance A and 3 litres of a $5M$ solution of substance B, is 6. Determine the yield of substance D.

30. 100 ml of a $0.5M$ solution of substance A and 400 ml of a $0.3M$ solution of substance B react as follows:

$$A + B \rightleftharpoons D + E.$$

Calculate the yield of substances D and E, when the equilibrium constant of the reaction is 5.

C. Ionic equilibrium

According to the classical theory of electrolytic dissociation, developed in the 1880s by Svante Arrhenius, part of an electrolyte dissolved in water falls into electrically charged particles, ions. In solution these particles have individual properties and unlike their parent molecules can take part in chemical reactions. The rate of a chemical reaction in a solution is therefore determined not by the concentration of the solute, but by the concentration of ions formed by this solute, these ions making up he active part of the whole dissolved substance. The degree of electrolytic dissociation is therefore very important. *The degree of electrolytic dissociation* (α) *is the ratio of the concentration of solute dissociated into ions to the total concentration of the solute in solution.* The total concentration of solute is often called *analytical concentration.* The process of electrolytic dissociation is presented in a general form like a reversible chemical reaction

$$AB \rightleftharpoons A^+ + B^-$$

where AB are undissociated molecules, and A^+ and B^- are ions.

If, in this equation, we regard the undissociated molecules as the starting reactants and the ions as the reaction products, and apply the law of chemical equilibrium, we derive a mathematical expression of the law of ionic equilibrium:

$$\frac{[A^+][B^-]}{[AB]} = K_{dis}.$$

The law of ionic equilibrium is a special case of the general law of chemical equilibrium. It reads as follows: *in solutions of weak electrolytes, in a state of ionic equilibrium, the ratio of the product of ion concentrations to the concentration of undissociated molecules is a constant known as the dissociation constant.* Using this law we can solve various problems connected with dissociation and interaction between substances in solutions of weak electrolytes.

Main propositions of the modern theory of electrolytic dissociation. The interaction of electrolyte ions in solution depends on the electrostatic forces: ions bearing oppo-

site charges are attracted and ions of like charge are repelled from one another. The electrostatic interaction depends on the nature of the electrolyte, its concentration in solution, and the dielectric constant of the solvent. The weaker the forces of electrostatic attraction between the ions of a given solute, the higher the possibility of interaction of these ions with ions of other substances.

The behaviour of an electrolyte in solution is determined not by the degree of its dissociation α, but by a specific real quantity which accounts for all interactions affecting the ion mobility, namely the ratio of the activity of a given substance to its overall concentration. This ratio is known as the *activity coefficient*, and designated by the letter f:

$$f=\frac{\text{activity}}{\text{overall concentration}}=\frac{a}{C}, \quad \text{whence } a=fC.$$

The activity coefficient, like α, can have various magnitudes, but cannot be greater than 1: $f \leqslant 1$.

Values of f and α are, as a rule, close to each other. Therefore, when dealing with dilute solutions of weak electrolytes, it is quite sufficient to substitute in the equation of ionic equilibrium the concentration of ions determined by the value of α. But in order to indicate that the activity a should in practice be used, the degree of dissociation is called *apparent* or *effective*.

We will now practise calculating the dissociation constant. To do so, one substitutes in the ionic equilibrium equation the equilibrium concentrations of ions and molecules and then does the necessary calculations. Equilibrium concentrations of all substances can be determined empirically or calculated by the apparent degree of their dissociation.

Example 1. The concentrations of H^+ and CH_3COO^- ions in a 0.1*M* solution of acetic acid are 0.00136 g-ion/litre. Determine the dissociation constant K_{dis} of CH_3COOH.

Solution. Set out the equation of dissociation of the acid and write the initial concentrations above and the equilibrium concentrations below:

$$\begin{array}{ccccc} 0.1 & & 0 & & 0 \\ CH_3COOH & \rightleftharpoons & H^+ & + & CH_3COO^- \\ 0.09864 & & 0.00136 & & 0.00136 \end{array}$$

Calculate the concentration of undissociated molecules by subtracting the concentration of either ion from the total concentration of the solution, since the number of moles of the dissociated acid is equal to the number of formed gram-ions of each ion:

$$0.1 - 0.00136 = 0.09864 \text{ mole/litre.}$$

Substitute these magnitudes in the formula:

$$K_{dis} = \frac{0.00136 \times 0.00136}{0.09864} = 1.88 \times 10^{-5}.$$

Example 2. Determine the dissociation constant K_{dis} of acetic acid, given that the apparent dissociation of its $0.1M$ solution is 1.36 per cent.

Solution. First determine the ion concentration in the given solution, assuming its concentration ($0.1M$) to be 100 per cent:

$$\begin{array}{l} 0.1 - 100\% \\ x - 1.36\% \end{array} \quad x = \frac{0.1 \times 1.36}{100} = 0.00136 \text{ g-ion/litre.}$$

Next determine K_{dis} in the same way as in the previous example.

Once the dissociation constant of a substance is known, reverse problems can be solved, i.e. concentrations of ions n solution can be found.

Example 3. Determine the concentrations of H^+ and CH_3COO^- ions in a $0.2M$ solution of acetic acid, given that the dissociation constant K_{dis} is 1.8×10^{-5}.

Solution. As in the previous example, set out the equation of acid dissociation and write the concentrations of the particles (in moles/litre and in g-ion/litre), designating the unknown by x:

$$\begin{array}{ccccc} & 0.2 & & 0 & 0 \\ CH_3COOH & \rightleftharpoons & H^+ & + & CH_3COO^- \\ & (0.2-x) & & x & x \end{array}$$

From the law of the ionic equilibrium we have

$$\frac{x^2}{(0.2-x)} = 1.8 \times 10^{-5}; \quad x^2 + 1.8 \times 10^{-5}x - 0.36 \times 10^{-5} = 0.$$

Solve the equation to obtain $x = 1.9 \times 10^{-3}$ g-ion/litre. Since acetic acid is very weak and low dissociated, the quantity $(0.2 - x)$ can be considered to be approximately equal to 0.2. Then the full quadratic equation turns into an incomplete equation and is solved as follows:

$$\frac{x^2}{0.2} = 1.8 \times 10^{-5}; \quad x = \sqrt{3.6 \times 10^{-6}} \approx$$

$$\approx 1.9 \times 10^{-3} \text{ g-ion/litre.}$$

Using the law of ionic equilibrium and given the dissociation constant, one can determine the apparent degree of dissociation.

Example 4. For acetic acid K_{dis} is 1.8×10^{-5}. Determine the apparent degree of dissociation of a $0.2M$ solution.

Solution. As in the previous example, we first determine the concentration of ions in the given solution and find that it is 1.9×10^{-3}. Next we determine the degree of dissociation

$$\alpha = \frac{1.9 \times 10^{-3} \times 100}{0.2} = 0.95 \text{ per cent.}$$

Once the dissociation constant is known, we can find the degree of dissociation of a solution of any concentration, and also determine how the apparent degree of dissociation or the concentration of ions of a given substance changes with dilution of the solution.

Example 5. How will the apparent degree of dissociation of a $0.2M$ solution of acetic acid change if the solution is diluted with water four-fold?

Solution. Using Table 4 in the Appendix, we find the dissociation constant of acetic acid (1.8×10^{-5}). We determine the degree of dissociation of the $0.2M$ solution following the method used in the previous example. Next, we

find the concentration of the acid after dilution: 0.2 : 4 = = 0.05*M*. As in the previous example, we determine the ion concentration in the solution:

$$\frac{x^2}{0.05} = 1.8 \times 10^{-5}: \quad x = 9.5 \times 10^{-4};$$

$$\alpha = \frac{9.5 \times 10^{-4} \times 100}{0.05} = 1.9 \text{ per cent.}$$

Divide 1.9 by α of the 0.2*M* solution (0.95%) to obtain the answer:

$$1.9 : 0.95 = 2 \text{ times.}$$

If we write the first equations of this and the previous examples in the general form and replace the concentration x of the ion by the expression $C\alpha$ (the product of the concentration of the solution and the degree of its dissociation expressed in fractions, not in per cent), we obtain the following:

$$\frac{(C\alpha)^2}{C} = K_{\text{dis}}, \quad \text{or, after cancelling out:}$$

$$C\alpha^2 = K_{\text{dis}}$$

whence

$$\alpha = \sqrt{\frac{K_{\text{dis}}}{C}}.$$

This formula is used to solve problems similar to the examples given above and is the expression of Ostwald's *dilution law* for binary (dissociating only into two ions) weak electrolytes for which $(1 - \alpha)$ can be considered to be practically unity. The exact mathematical expression of the dissociation constant of weak binary electrolytes has the following form:

$$K_{\text{dis}} = \frac{\alpha^2 C}{(1 - \alpha)}.$$

In solving similar problems, we usually deal with very small magnitudes, which, for the sake of convenience, could be better written in the exponential form, i.e. in the form of two cofactors, one of which is 10 raised to any negative

power. During calculations it is not recommended to convert magnitudes thus expressed into decimals with a large number of zeros. This will only interfere with routine calculations and cause errors. (Such operations are unavoidable only in summation and subtraction.) For example, the equation in Example 5 should be solved as follows:

$$x^2 = 0.05 \times 1.8 \times 10^{-5} = 5 \times 10^{-2} \times 1.8 \times 10^{-5} = 9 \times 10^{-7};$$

$$x = \sqrt{9 \times 10^{-7}} = \sqrt{90 \times 10^{-8}} = 9.5 \times 10^{-4}.$$

Further calculations are as follows:

$$x = \frac{9.5 \times 10^{-4} \times 100}{5 \times 10^{-2}} = \frac{9.5}{5} = 1.9\%.$$

All operations are performed mentally and only the intermediate results are written down. Roots should be found with a slide rule, tables, or calculators.

An analyst often has to calculate changes in the concentrations of ions in a solution into which an electrolyte containing the common ion is added. The law of ionic equilibrium is used to solve such problems. The concentrations of ions after adding the second electrolyte are substituted into the main equation of the ionic equilibrium. The required concentrations are designated by x. If the calculations are approximate, the initial concentrations of the ions, whose concentrations strongly increase after addition of the second electrolyte, are not considered.

Example 6. Determine the concentration of the hydrogen ion in a 0.1*N* solution of CH_3COOH, whose one litre contains 8.2 g of anhydrous sodium acetate.

Solution. Write down the equations of dissociation of acetic acid and sodium acetate:

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

$$CH_3COONa \rightleftharpoons Na^+ + CH_3COO^-.$$

The CH_3COO^- ion is found in both electrolytes. First determine the concentration of sodium acetate:

$$8.2 : 82 = 0.1 \text{ mole/litre}$$

where 82 is the molecular mass of CH_3COONa.

Write out the equation of ionic equilibrium for acetic acid:

$$\frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = K_{dis}.$$

We find the numerical values of all quantities in the formula: $[H^+]$ the sought quantity, which we express as x; $[CH_3COO^-]$ equals the sum of concentrations of this ion in solutions of acetic acid and sodium acetate. The first concentration can be disregarded since it is negligible compared with the second concentration, because acetic acid is weak and very poorly dissociated while the $0.1N$ solution of sodium acetate, like dilute solutions of most salts, is well dissociated. Therefore $[CH_3COO^-]$ can be assumed to be equal to its concentration in the $0.1N$ solution of CH_3COONa. Calculate this concentration by multiplying the concentration of CH_3COONa by the degree of dissociation taken from Table 5 of the Appendix (for $0.1N$ solutions of salts of type A^+B^-). Hence,

$$[CH_3COO^-] = 0.1 \times 0.86 = 0.086 \text{ mole/litre}$$

where 0.86 is the apparent degree of dissociation of salts of the A^+B^- type expressed not in per cent but in parts of a whole; $[CH_3COOH] = 0.1$ mole/litre (from the condition of the problem); and K_{dis} is 1.8×10^{-5} (from Table 4, see Appendix).

Substitute all magnitudes in the formula to obtain

$$\frac{x \cdot 0.086}{0.1} = 1.8 \times 10^{-5}; \quad x = 2.1 \times 10^{-5} \text{ mole/litre}.$$

If accuracy is not important, the apparent degree of dissociation for the added electrolyte can be disregarded and assumed to be unity. The solution of the problem will then be simplified:

$$\frac{x \cdot 0.1}{0.1} = 1.8 \times 10^{-5}, \quad \text{whence } x = 1.8 \times 10^{-5}.$$

This answer differs slightly from the previous one, but its accuracy is sufficient in most cases.

Example 7. How will the apparent degree of dissociation of a 0.1*M* solution of acetic acid change if 8.2 g of anhydrous sodium acetate are added to one litre of the solution (disregard the change in volume caused by the addition)?

Solution: First find the degree of dissociation of the 0.1*M* solution of CH_3COOH following the procedure described in Example 4 or taking it from the tables. Determine $[CH_3COO^-]$ in the solution after adding CH_3COONa by the method described in Example 6. Determine α of the 0.1*M* solution of the acid containing 0.1 mole/litre of sodium acetate:

$$\alpha = \frac{2.1 \times 10^{-5} \times 100}{0.1} = 2.1 \times 10^{-2} = 0.021\%.$$

Divide α of the 0.1*M* solution of the acid (about 1.4%) by the number determined:

$$1.4 : 0.021 = 67 \text{ times (decrease).}$$

Problems

Note: Wherever values of α, K_{dis} or solubilities are not given in the problem, they can be found in the Appendix or special reference books. Unless otherwise specified the degrees of dissociation of substances in dilute solutions should be assumed to be 100%.

1. How many gram-ions of H^+ and Cl^- will be obtained by the complete dissociation of one mole of hydrochloric acid?
2. How many gram-ions of Na^+ and Cl^- will be obtained by the complete dissociation of two moles of sodium chloride?
3. How many gram-ions of H^+ and SO_4^{2-} will be obtained by the complete dissociation of one mole of sulphuric acid?
4. How many gram-ions of Ba^{2+} and OH^- will be obtained by the complete dissociation of one mole of barium hydroxide?

5. How many gram-ions of Al^{3+} and SO_4^{2-} will be obtained by the complete dissociation of 0.01 mole of aluminium sulphate?

6. How many gram-ions of Na^+ and PO_4^{3-} will be obtained by the complete dissociation of 0.5 mole of sodium phosphate?

7. How many moles of barium chloride will be produced by the combination of 0.5 g-ion of Ba^{2+} with 1 g-ion of Cl^-?

8. How many moles of lead chloride will be obtained by the combination of 0.02 g-ion of Pb^{2+} with 0.04 g-ion of Cl^-?

9. How many moles of phosphoric acid will be produced by the combination of 0.3 g-ion of H^+ with 0.1 g-ion of PO_4^{3-}?

10. How many moles of calcium phosphate are formed by the combination of 0.6 g-ion of Ca^{2+} with 0.4 g-ion of PO_4^{3-}?

11. The effective concentration of the hydrogen ion in a 1*N* solution of HCl is 0.78 g-ion/litre. Determine the apparent degree of dissociation.

12. Determine the apparent degree of dissociation of copper sulphate in a 0.1*M* solution, given that the effective concentration of the sulphate ion is 0.04 g-ion/litre.

13. The concentration of the hydrogen ion in a solution containing 3.65 g of HCl in one litre is 0.00009 g-ion/ml. What is the apparent degree of dissociation of HCl?

14. Determine the degree of dissociation of ammonium hydroxide in a 1.028*M* solution if the effective concentration of the OH^- ion is 0.004112 g-ion/litre.

15. Determine the effective concentration of the hydrogen ion in a 3 per cent solution of acetic acid when α is 0.6 per cent.

16. Determine the effective concentration of the CH_3COO^- ion in a 0.001*M* solution of CH_3COOH, provided α is 12.4%.

17. How many grams of the H^+ ion are contained in 100 ml of a 0.1*M* solution of hydrochloric acid and acetic acid?

18. How many grams of H^+ and Cl^- ions and undissociated molecules of HCl are contained in 500 ml of a 1*M* solution?

19. How many grams of the Na^+ ion are contained in 500 ml of a 2*M* solution of NaOH if α is 60 per cent?

20. There are equal volumes of 0.1*M* solutions of acetic and hydrocyanic acids. Which of them contains the greater amount of the H^+ ion? How much greater?

21. How many grams and gram-ions of Ba^{2+} are contained in 250 ml of a saturated solution of barium sulphate?

22. Determine the concentration (in g-ion/litre and in g/litre) of the Ca^{2+} ion in saturated at 20°C solution of: (a) calcium hydroxide, (b) calcium sulphate, (c) calcium carbonate.

23. Write down the equation of dissociation of formic acid. Work out the expression of the law of ionic equilibrium for this acid, designating the concentrations of particles by bracketed formulas.

24. Follow the instructions given in Problem 23 for the dissociation of hydrosulphuric acid (first and second dissociations).

25. Do the same for hydroxides of ammonium, magnesium, and aluminium.

26. Do the same for magnesium carbonate, lead chloride, and aluminium sulphate.

27. Determine the dissociation constant for acetic acid if the apparent degree of dissociation of a 0.2*M* solution is 0.95 per cent.

28. The apparent degree of dissociation of a 0.001*M* solution of HCOOH is 36.8 per cent. What is the dissociation constant of the acid?

29. Determine the dissociation constant of nitrous acid, when α of a 0.1*M* solution is 6.6 per cent.

30. Determine the dissociation constant of hydrocyanic acid by its α.

31. Determine the dissociation constant of H_2CO_3 by the first dissociation of a 0.1*M* solution ($\alpha = 0.2$ per cent).

32. If α of a 0.2*M* solution of hypochlorous acid is 0.053 per cent, determine its dissociation constant.

33. Does acetic acid obey the law of ionic equilibrium if α of its solutions of various molarity are as follows:

M	1	0.5	0.1
α, %	0.4	0.6	1.36

34. The apparent degrees of dissociation of hydrochloric acid solutions of various molarity are as follows:

M	1	0.5	0.1	0.01
α, %	78	86	92	99.7

Does hydrochloric acid obey the law of ionic equilibrium?

35. Calculate the dissociation constant of ammonium hydroxide by its apparent degree of dissociation:

M	1	0.5	0.1
α, %	0.43	0.60	1.34

36. Can we speak about the dissociation constant of NaOH (and why) if it is known that the apparent degrees of dissociation of its solutions are as follows:

M	1.0	0.5	0.1	0.01
α (in parts of a whole)	0.73	0.795	0.92	0.966

37. Determine the effective concentration of the hydrogen ion in a $0.6M$ solution of CH_3COOH if K_{diss} is 1.8×10^{-5}.

38. Determine the effective concentration of H^+ and NO_2^- ions in a $0.2M$ solution of HNO_2, taking its dissociation constant from Table 4 in the Appendix.

39. How will the concentration of the OH^- ion change in a $0.2M$ solution of NH_4OH if it is diluted with five volumes of water?

40. How will the concentration of the hydrogen ion change in a $1M$ solution of HCOOH if it is diluted with four volumes of water?

41. How many grams of H^+ and $HCOO^-$ ions do 250 ml of a $0.5M$ solution of HCOOH contain?

42. How many grams of OH^- ion do 100 ml of a $0.05M$ solution of NH_4OH contain?

43. Calculate the degree of dissociation of a $0.1M$ solution of HCOOH.

44. How will the apparent degree of dissociation of a $0.1M$ solution of hydrocyanic acid change if it is diluted with ten volumes of water?

45. The dissociation constant of HClO is 4×10^{-8}. Determine the apparent degree of dissociation for solutions of the acid having the following concentrations: $1M$, $0.5M$, $0.1M$, and $0.05M$.

46. Calculate the degree of dissociation of a 0.1*M* solution of hydrogen sulphide by its first and second dissociations and the dissociation constant.

47. How will the apparent degree of dissociation of a 0.1*M* solution of NH_4OH change if water is added to dilute it to the following concentrations (in mole/litre): 0.05, 0.02, 0.01, 0.008, and 0.001?

48. Construct a curve showing the dependence of the apparent degree of dissociation of a 0.1*M* solution of CH_3COOH on dilution in the range of concentrations from 0.1*M* to 0.001*M*.

49. Determine the concentration of the hydrogen ion in a 0.1*M* solution of HCOOH containing 3.4 g of sodium formiate in one litre.

50. Determine the hydrogen ion concentration in a 1*M* solution of CH_3COOH containing 0.41 g of anhydrous sodium acetate in 100 ml.

51. Add 100 ml of sodium acetate solution containing 1.64 g of anhydrous CH_3COONa to 100 ml of a 0.2*M* solution of CH_3COOH. Determine the hydrogen ion concentration in the resultant solution.

52. Place 4.10 g of anhydrous sodium acetate and 63.6 ml of acetic acid solution (density, 1.040 g/cc) in a 500-ml volumetric flask and add water to the mark. What is the hydrogen ion concentration in the resultant solution?

53. Determine the apparent degree of dissociation of a 0.2*M* solution of HCOOH, whose 250 ml contain 1.7 g of sodium formiate.

54. Dissolve 2.05 g of anhydrous sodium acetate in a 250-ml volumetric flask in a 0.5*M* solution of CH_3COOH, and add the acid to the mark. What is the apparent degree of dissociation of the resultant solution?

55. How will the apparent degree of dissociation of a 0.05*M* solution of CH_3COOH change if 0.082 g of anhydrous sodium acetate is added to 100 ml of the solution?

56. How will the apparent degree of dissociation of formic acid change if 100 ml of sodium formiate solution containing 3.4 g of the salt are added to 400 ml of 0.5*M* solution?

57. Determine the apparent degree of dissociation of solutions, one of which contains 3.4 g of ammonia and 2.68

g of ammonium chloride in one litre, and the other 6.8 g of ammonia and 2.68 g of ammonium chloride in the same amount of solution.

58. Determine the apparent degree of dissociation of nitrous acid, whose 0.05*M* solution contains 6.9 g of sodium nitrite in one litre, if the apparent degree of dissociation of the salt in this solution is 88 per cent.

59. To what level should the concentration of sodium acetate in a 0.1*M* solution of CH_3COOH be raised to lower its apparent degree of dissociation to 0.05 per cent?

60. How many grams of sodium acetate should be dissolved in 100 ml of a 0.1*M* solution of CH_3COOH to bring its apparent degree of dissociation to 0.05 per cent?

D. Equilibrium in saturated solutions

Equilibrium in a saturated solution of an electrolyte above its precipitate obeys the law of the solubility product. The law reads as follows: *the product of concentrations of ions in a saturated solution of a sparingly soluble electrolyte in a state of equilibrium is a constant known as the solubility product*:

$$SP_{A_mB_n} = [A^+]^m [B^-]^n$$

where $SP_{A_mB_n}$ is the solubility product of the substance A_mB_n; $[A^+]$ and $[B^-]$ are concentrations of ions in a saturated solution; m and n are quantities of atoms or atomic groupings in a molecule of the given substance.

Only sparingly soluble substances obey this law. The degree of dissociation of saturated solutions of very low concentrations is usually assumed to be 100 per cent.

To calculate the solubility product of a given substance it is necessary to multiply the concentrations of ions in the saturated solution, raised to the corresponding power. The concentrations of ions, which should be expressed in g-ion/litre, are determined from the solubility of the given substance. *The solubility of a substance is the maximum number of grams of the substance that can dissolve at a given temperature in* 100 *g of solvent.*

If one wants to convert solubility into molar concentration, one should first determine the number of grams of the given substance contained in one litre of saturated solution. To do so, the solubility should be multiplied by ten, the error being insignificant. To determine the molarity of a saturated solution, the quantity obtained should be divided by the molecular mass of the solute.

Example 1. Determine the concentrations of Ag^+ and Br^- ions in a saturated solution of AgBr if its solubility is known.

Solution. The solubility of AgBr at 20°C is 1×10^{-5} g in 100 g of water. Determine the molarity of the saturated solution:

$$M = \frac{1 \times 10^{-5} \times 10}{188} = 5.3 \times 10^{-7} \text{ mole/litre.}$$

Since AgBr dissociates to give one Ag^+ and one Br^- ion, the concentration of either is 5.3×10^{-7} g-ion/litre.

Example 2. Determine the solubility product of AgBr.

Solution. Proceed as in the previous example and determine the concentrations of Ag^+ and Br^- in the saturated AgBr solution, which are 5.3×10^{-7} g-ion/litre. Write down the equation of the dissociation:

$$AgBr \rightleftarrows Ag^+ + Br^-.$$

From the equation it follows:

$$SP_{AgBr} = [Ag^+]\,[Br^-] = (5.3 \times 10^{-7})^2 = 2.8 \times 10^{-13}.$$

Example 3. Determine $SP_{Ag_2C_2O_4}$ if the solubility of $Ag_2C_2O_4$ is 3.27×10^{-3}.

Solution. Determine the molarity of a saturated solution of $Ag_2C_2O_4$:

$$M_{Ag_2C_2O_4} = \frac{3.27 \times 10^{-3} \times 10}{304} = 1.076 \times 10^{-4} \text{ mole/litre.}$$

The equation of dissociation of silver oxalate

$$Ag_2C_2O_4 \rightleftarrows 2Ag^+ + C_2O_4^{2-}$$

shows that the concentration of the $C_2O_4^{2-}$ ion in the saturated solution equals its molarity, while the concentration of Ag^+ is twice as much, i.e. $1.076 \times 10^{-4} \times 2 = 2.15 \times \times 10^{-4}$ g-ion/litre. Whence:

$$SP_{Ag_2C_2O_4} = [Ag^+]^2[C_2O_4^{2-}] = (2.15 \times 10^{-4})^2 1.076 \times 10^{-4} = 5 \times 10^{-12}.$$

Example 4. Determine the concentration of Ag^+ and $C_2O_4^{2-}$ ions in a saturated solution of silver oxalate if its solubility product is known.

Solution. Let us designate the molarity of a saturated solution of silver oxalate by x. Then, as in the previous example, the concentration of the $C_2O_4^{2-}$ ion will be x g-ion/litre while the concentration of Ag^+ will be $2x$. Substitute these in the equation of the solubility product:

$$SP_{Ag_2C_2O_4} = (2x)^2 x = 4x^3.$$

Take $SP_{Ag_2C_2O_4}$ from Table 6 of the Appendix to obtain the final formula: $4x^3 = 5 \times 10^{-12}$. Solve this equation to find $x = 1.077 \times 10^{-4} M$. The same quantity, expressed in g-ion/litre, characterizes the concentration of $C_2O_4^{2-}$, while the concentration of Ag^+ is twice as much, i.e. $2.15 \times \times 10^{-4}$ g-ion/litre.

Example 5. Determine the solubility of silver oxalate from its solubility product.

Solution. Proceed as in the previous example to find the molarity of a saturated solution of silver oxalate, and then multiply the quantity obtained by the molar mass of silver oxalate. Since solubility is calculated for 100 g of water and not for one litre, divide by 10:

$$\frac{1.077 \times 10^{-4} \times 304}{10} = 3.27 \times 10^{-3} \text{ g/100}.$$

The solubility product can be used to decide whether precipitation occurs as a result of the mixing together of solutio s First the resultant concentrations of precipitating ions re determined. The concentrations obtained are multiplied by one another and the product is compared with the solubility product of the substance that precipitates. If the product of the concentrations of the ions is much greater than the solubility product, the precipitation occurs. If

the product of the concentrations does not exceed the solubility product by more than one hundred times, the solution becomes supersaturated but precipitation does not occur for a considerable time.

Example 6. Decide if a precipitation occurs on the mixing together of 10 ml of a $0.02N$ solution of $CaCl_2$ and 5 ml of a $0.1N$ solution of K_2CrO_4.

Solution. The reaction equation

$$CaCl_2 + K_2CrO_4 \rightleftharpoons CaCrO_4 + 2KCl$$

shows that to solve the problem one must know the concentrations of Ca^{2+} and CrO_4^{2-} ions. Convert normality into molarity:

$$0.02N\ CaCl_2 = 0.01M; \quad 0.1N\ K_2CrO_4 = 0.05M.$$

Determine the ion concentrations after mixing the solutions:

$$[Ca^{2+}] = \frac{0.01 \times 10}{(10+5)} = 6.7 \times 10^{-3}\ \text{g-ion/litre}$$

$$[CrO_4^{2-}] = \frac{0.05 \times 5}{(10+5)} = 1.67 \times 10^{-2}\ \text{g-ion/litre.}$$

Whence

$$[Ca^{2+}]\ [CrO_4^{2-}] = 6.7 \times 10^{-3} \times 1.7 \times 10^{-2} = 11.4 \times 10^{-5} = 1.14 \times 10^{-4}.$$

Consult Table 6 to find $SP_{CaCrO_4} = 2.3 \times 10^{-2}$. Since 1.14×10^{-4} is less than 2.3×10^{-2}, there will be no precipitation, because the resultant solution will be unsaturated. For the sake of convenience, convert the quantities with negative exponents so that all exponents are the same. In our case $2.3 \times 10^{-2} = 230 \times 10^{-4}$. The comparison of quantities with equal exponents becomes much easier: 230×10^{-4} is greater than 1.14×10^{-4}.

When the volume of one of the solutions mixed together is much greater than that of the other solution, we can assume that the concentration of the solution present in the greater quantity will not practically change. For example, if we mix 100 ml of a solution with 1 ml of another, the concentration of the former will remain virtually unchanged, while

the concentration of the latter solution will decrease about 100 times.

If the condition of a problem does not specify the concentrations of the solutions to be mixed, indicating only that one of them (or both) are saturated, their concentrations can be found from the solubility product in Table 6 (see Example 4).

Problems in which a reagent is added to a mixture of ions (with the result of precipitation) should also be solved using the law of the solubility product. It follows from the law that: *two ions in solution will precipitate simultaneously by the action of one precipitating agent only when their concentrations relate to each other as the solubility products of the precipitates formed.*

Example 7. What should the ratio of the concentrations of Sr^{2+} and Ba^{2+} ions be, if we want their sulphates to precipitate simultaneously upon the addition of the SO_4^{2-} ion?

Solution. Consult Table 6 to find the solubility products of the sulphates and calculate

$$\frac{[Sr^{2+}]}{[Ba^{2+}]} = \frac{3.6 \times 10^{-7}}{1 \times 10^{-10}} = \frac{3.6}{10^{-3}} = 3600.$$

It follows that sulphates of strontium and barium will simultaneously precipitate on the condition that $[Sr^{2+}]$ is 3600 times greater than $[Ba^{2+}]$. If $\frac{[Sr^{2+}]}{[Ba^{2+}]} > 3600$, strontium sulphate starts precipitating and will continue to do so until the ratio of the concentrations of the strontium and barium ions becomes 3600. When this condition is fulfilled, both substances start to precipitate simultaneously. If, however, $\frac{[Sr^{2+}]}{[Ba^{2+}]} < 3600$, barium sulphate will precipitate first, and will continue precipitating alone until this ratio becomes 3600, after which both substances will precipitate simultaneously.

Example 8. A solution contains ions of barium and strontium whose concentrations are (in g-ion/litre) 0.0003 and 1 respectively. Which ion will precipitate first if K_2CrO_4 solution is gradually added?

Solution. Use Table 6 to find the following:

$$\frac{SP_{SrCrO_4}}{SP_{BaCrO_4}} = \frac{3.6 \times 10^{-5}}{2.3 \times 10^{-10}} = 160{,}000.$$

The ratio of the concentrations of the ions in the given solution is $1/(3 \times 10^4) = 3300$. This means that the ratio of the concentrations of the ions is much less than the ratio of the solubility products of the precipitates. Hence, barium chromate will be the first to precipitate.

It is no less important to know how the precipitation process depends on the conditions of the reaction, for example, the medium. This problem is often solved using the solubility product as well. An analyst often has to precipitate cations with hydrogen sulphide. Problems of the following two types usually occur: (a) determination of the concentration of a cation which remains in solution at a given concentration of hydrogen ion; (b) determination of the possibility of precipitating one cation in the presence of another; (c) determination of the hydrogen ion concentration in solution from which a given cation should be completely precipitated. To solve problems involving doubly charged cations, the ollowing formula should be used:

$$\frac{SP_{MeS}}{[Me^{2+}]} = \frac{K_1 K_2 [H_2S]}{[H^+]^2}$$

where SP_{MeS} is the solubility product of the sulphide of a doubly charged cation; K_1 and K_2 are the first and the second dissociation constants of hydrogen sulphide respectively; $[H_2S]$ is the hydrogen sulphide concentration in a saturated solution, in mole/litre; $[Me^{2+}]$ is the concentration of the precipitated doubly charged cation in the equilibrium state in g-ion/litre; and $[H^+]$ is the hydrogen ion concentration in solution from which the cation will be precipitated, in g-ion/litre.

Since K_1, K_2, and $[H_2S]$ in a saturated solution are constants, their product can be calculated beforehand and put into the numerator of the ratio. The formula will then be simplified to

$$\frac{SP_{MeS}}{[Me^{2+}]} = \frac{1.08 \times 10^{-23}}{[H^+]^2}$$

from which it follows that

$$[Me^{2+}] = \frac{SP_{MeS}[H^+]^2}{1.08 \times 10^{-23}} \quad (1)$$

and

$$[H^+] = \sqrt{\frac{[Me^{2+}] \times 1.08 \times 10^{-23}}{SP_{MeS}}}. \quad (2)$$

Formula (1) can be used to determine the concentration of the cation in solution at a given concentration of the hydrogen ion, and formula (2) is suitable for the determination of the hydrogen ion concentration at which the ion of a given metal can be quantitatively precipitated.

The rule of the solubility product can be used to solve many important problems concerning the transformation of one precipitate into another and the necessary concentrations of the reagents to achieve this.

Example 9. What is the least concentration of NaCl at which AgBr precipitate can be converted into AgCl?

Solution. AgCl will precipitate in the reaction

$$AgBr + NaCl \rightleftharpoons AgCl + NaBr$$

if $[Ag^+]\,[Cl^-] > SP_{AgCl}$. Since the solution above the AgBr precipitate is saturated,

$$[Ag^+] = \sqrt{SP_{AgBr}} = 5.7 \times 10^{-7}.$$

SP_{AgCl} is 1.7×10^{-10} (see Table 6 in the Appendix). Substitute the data in the SP formula to find the following:

$$[Cl^-] = \frac{1.7 \times 10^{-10}}{5.7 \times 10^{-7}} = 3 \times 10^{-4} \text{ g-ion/litre.}$$

The concentration of NaCl, in mole/litre, will be the same. If [NaCl] is less than the quantity found, even partial conversion of silver bromide into the chloride is impossible. If we want to accelerate the conversion of AgBr into AgCl, the concentration should be increased 10-100 times and the bromide ions which have accumulated should be removed from the solution.

*Problems**

1. Write down the mathematical expression of the solubility product of silver chloride, calcium sulphate, and copper sulphide.
2. Write down the mathematical expression of the solubility product of silver bromide, barium sulphate, nickel sulphide, and calcium carbonate.
3. Write down the mathematical expression of the solubility product of lead chloride, silver chromate, mercury iodide, and calcium phosphate.
4. Write down the mathematical expression of the solubility product of silver sulphate, aluminium phosphate, and arsenic sulphide.
5. What is the molarity of a saturated solution of $BaSO_3$ if its solubility is 0.02?
6. What is the molarity of a saturated solution of $PbSO_4$ whose solubility under given conditions is 4.1×10^{-3}?
7. What is the molarity of a saturated solution of $BaCrO_4$ whose solubility is 3.4×10^{-4}?
8. What is the molarity of a saturated solution of $SrSO_4$ whose solubility is 1.14×10^{-2}?
9. What are the concentrations, in g-ion/litre, of Ag^+ and Cl^- ions in a saturated at 20°C solution of AgCl whose solubility is 1.5×10^{-4}?
10. Determine the concentration, in g-ion/litre, of Ca^{2+} and SO_4^{2-} ions in a saturated solution of $CaSO_4$, if its solubility is 0.2.
11. What is the concentration, in g-ion/litre, of Ca^{2+} and CrO_4^{2-} ions in a saturated solution of $CaCrO_4$, if we assume its solubility to be 2.34 and disregard its slightly incomplete dissociation?
12. A precipitate of calcium carbonate is shaken in water for a considerable time. What is the concentration, in g-ion/litre, of Ca^{2+} and CO_3^{2-} ions in the solution, if the solubility of $CaCO_3$ at a given temperature is 1.3×10^{-3}?
13. The solubility of $BaSO_4$ is 2.3×10^{-4}. Determine its solubility product.

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* Solubility is expressed in grams per 100 g of solvent.

14. Determine the solubility product of $CaCO_3$ if its solubility is 1.3×10^{-3}.

15. Determine the solubility product of $MgCO_3$ if its solubility is 2.67×10^{-2}.

16. Determine the solubility product of AgCl if its solubility at 25°C is 1.86×10^{-4}.

17. Determine the solubility product of $PbCl_2$ if its solubility under certain conditions is 0.445.

18. Determine the solubility product of Ag_2CrO_4 if its solubility is 2.6×10^{-3}.

19. What is the solubility product of $Zn(OH)_2$ if under certain conditions its solubility is 2.2×10^{-5}?

20. What is the solubility product of $PbBr_2$ if its solubility is 0.427?

21. Determine the solubility product of As_2S_3 if its solubility is 2×10^{-5}.

22. Determine the solubility product of Ag_2CO_3 if its solubility at 25°C is 3.5×10^{-3}.

23. Determine the degree of saturation* of a solution of $CaSO_4$ in which the concentration of Ca^{2+} is 0.008 g-ion/litre.

24. The concentration of Mg^{2+} in a solution of $MgCO_3$ is 3×10^{-3} g-ion/litre. Determine the degree of saturation in the solution.

25. A solution of $PbSO_4$ contains 1.5×10^{-4} g-ion/litre of SO_4^{2-}. Determine the saturation degree of the solution.

26. A solution of $SrCrO_4$ contains 6×10^{-3} g-ion/litre of CrO_4^{2-}. Will its concentration increase if we shake the solution with strontium chromate precipitate?

27. What is the degree of saturation of a solution of Ag_2CrO_4 containing 1×10^{-4} g-ion/litre of CrO_4^{2-}?

28. A solution of $Ag_2Cr_2O_7$ contains 7.4×10^{-3} g-ion/litre of Ag^+. What is the degree of saturation of the solution?

29. The concentration of Ag^+ in a solution of Ag_3AsO_4 is 2.5×10^{-5} g-ion/litre. Determine the degree of saturation of the solution.

30. What is the degree of saturation of a solution of Ag_3PO_4 which contains 1.6×10^{-5} g-ion/litre of PO_4^{3-}?

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* The degree of saturation indicates whether a solution is unsaturated, saturated, or supersaturated (see Problems 23-44).

31. Determine the concentration of ions (in g-ion/litre) in a saturated solution of $BaCO_3$ by its solubility product.

32. Determine the ion concentrations (in g-ion/litre) in a saturated solution of $CaSO_4$.

33. Determine the ion concentrations (in g-ion/litre) in a saturated solution of $BaSO_4$ by its solubility product.

34. How many gram-ions of Ag^+ are contained in one litre of saturated solutions of AgCl, AgBr, AgI?

35. Determine the concentration of ions, in g-ion/litre, in a saturated solution of $PbCl_2$.

36. How many gram-ions of Ag^+ and CrO_4^{2-} are contained in one litre of a saturated solution of Ag_2CrO_4?

37. Determine the solubility of zinc carbonate by its solubility product.

38. Determine the solubility of magnesium oxalate by its solubility product.

39. Determine the solubility of $PbCl_2$ by its solubility product.

40. Determine the solubility of CaF_2 by its solubility product.

41. Which saturated solution, of AgCl or of $PbCl_2$, contains the greater quantity of chlorine (in g-ion/litre)? How much greater?

42. There are two saturated solutions, of lead sulphate and lead phosphate. In which of them is the lead ion concentration greater (in g-ion/litre)? How much greater?

43. Determine, by their solubility products, whether $Cr(OH)_3$ or $Zn(OH)_2$ has greater solubility. How do their solubilities compare?

44. How many grams of S^{2-} are contained in 100 ml of saturated solutions of CuS and As_2S_3?

45. 10 ml of a 0.01*M* solution of sulphuric acid are added to 10 ml of a 0.01*M* solution of $CaCl_2$. Does any substance precipitate?

46. Equal volumes of 0.02*N* solutions of $SrCl_2$ and K_2CrO_4 are mixed. Does any substance precipitate?

47. 5 ml of a 0.1*N* solution of Na_2SO_4 are added to 10 ml of a 0.01*N* solution of $BaCl_2$. Does any substance precipitate?

48. 1 ml of a 0.001*M* solution of sulphuric acid is added

to 100 ml of a 0.001*N* solution of $PbCl_2$. Does any precipitation occur?

49. A drop of sulphuric acid (density, 1.080 g/cc) is added to 100 ml of a 0.01*M* solution of $CaCl_2$. Does any substance precipitate?

50. Five drops of HCl solution (density, 1.018 g/cc) are added to 100 ml of a 0.05*N* solution of $AgNO_3$. Does any substance precipitate?

51. Two volumes of a 0.1*N* solution of $(NH_4)_2CO_3$ are added to three volumes of a 0.1*N* solution of $Ca(NO_3)_2$. Will any substance precipitate?

52. One volume of hydrogen sulphide water is added to ten volumes of a 0.1*N* solution of $ZnSO_4$. Will any substance precipitate?

53. 5 ml of hydrogen sulphide water are added to 50 ml of a 0.2*M* solution of $CuSO_4$. Will any substance precipitate?

54. 5 ml of gypsum water are added to 15 ml of a 0.02*N* solution of $SrCl_2$. Will any substance precipitate?

55. Mixed are equal volumes of a saturated solution of $PbCl_2$ and gypsum water. Will any substance precipitate?

56. Lead is precipitated from a lead nitrate solution by adding sodium sulphate. The precipitate is separated on a filter. One volume of a 0.2*N* solution of ammonium carbonate is added to ten volumes of the filtrate. Does lead carbonate precipitate?

57. What is the ratio of the concentrations of barium and strontium ions in solution if both sulphates precipitate simultaneously on addition of SO_4^{2-}?

58. What should the ratio of the concentrations of SO_4^{2-} and CrO_4^{2-} ions be if we want to precipitate simultaneously both ions by adding Pb^{2+} to their solution?

59. A solution contains chloride and bromide ions, their concentration being 0.01 g-ion/litre each. A drop of a dilute solution of a silver salt is added to precipitate a substance. What is this substance?

60. A minute quantity of CrO_4^{2-} is added to a solution containing Pb^{2+} and Ba^{2+} in equal concentrations. What substance will precipitate first?

61. How much greater should the concentration of either Ca^{2+} or Sr^{2+} ion be than that of the other if we want both

carbonates to be formed simultaneously on the addition of CO_3^{2-} to the solution?

62. A solution contains $C_2O_4^{2-}$ and CrO_4^{2-} ions. The concentration of which ion should be greater, and how much greater, if we want lead oxalate and lead chromate to precipitate simultaneously?

63. The concentration of Br^- in a solution is 10,000 times higher than that of I^-. Ag^+ is added to the solution. Which ion precipitates first?

64. A solution contains Ba^{2+} in a quantity 100 times less than that of Sr^{2+}. CrO_4^{2-} is added. Which substance precipitates first?

65. The concentration of Ba^{2+} is 0.1 g-ion/litre. What should the concentration of Pb^{2+} be if we want the chromates of both ions to precipitate simultaneously?

66. The concentration of SO_4^{2-} in solution is 0.01 g-ion/litre. What should the concentration of CrO_4^{2-} be if we want sulphate and chromate to precipitate simultaneously on the addition of Ba^{2+}?

67. 100 ml of a solution contain 1 g of $CaCl_2$ and 1 g of $Sr(NO_3)_2$. An insignificant quantity of sodium carbonate is added to the solution. A precipitate falls out. What is this precipitate?

68. A drop of concentrated sulphuric acid is added to 50 ml of a solution containing 0.05 g of $Ca(NO_3)_2$ and 0.05 mg of barium chloride. Will any substance precipitate? In what sequence will the substances precipitate?

69. What is the least concentration of sodium sulphate at which lead chromate is converted into the sulphate?

70. Calcium oxalate is converted into the carbonate. What is the least concentration of sodium carbonate at which such a conversion becomes possible?

71. At what concentration of sodium chloride can silver thiocyanide be converted into silver chloride?

72. Strontium chromate should be converted into its sulphate. What is the reagent and its lowest concentration which can be used to achieve this object?

73. Strontium sulphate should be converted into its carbonate. What is the reagent and its lowest concentration which can be used to achieve this?

74. High concentration soda solution is added to a mixture

of sulphates of calcium, strontium, and barium. What will happen to the precipitate? Explain.

75. What quantity of Pb^{2+} (in g-ion/litre) will remain unprecipitated by hydrogen sulphide passed into a solution containing 0.3 g-ion/litre of the H^+ ion?*

76. Determine the concentration of Cd^{2+} in solution after precipitation with hydrogen sulphide, if the hydrogen ion concentration is 0.4 g-ion/litre.

77. A solution containing 0.3 g-ion/litre of H^+ also contains Fe^{2+} and Cu^{2+} ions. Hydrogen sulphide is passed to saturate the solution. What substance will be precipitated?

78. A solution containing 0.05 g-ion/litre of H^+ also contains Cd^{2+} and Ni^{2+} ions. What substance will be precipitated by hydrogen sulphide?

79. Can hydrogen sulphide precipitate Fe^{2+} from a solution containing 0.2 g-ion/litre of H^+?

80. Can hydrogen sulphide precipitate practically all Cd^{2+} from a solution containing 0.5 g-ion/litre of H^+?

81. A solution containing 0.5 g-ion/litre of H^+ also contains Pb^{2+} and Cd^{2+}. The concentration of which ion will be greater (and how much greater) after precipitation with hydrogen sulphide if the hydrogen ion concentration remains constant during precipitation?

82. A solution contains Sn^{2+} and Pb^{2+} ions. Which of them will remain in the greater quantity (and how much greater) if the hydrogen ion concentration during the precipitation with hydrogen sulphide is 0.2 g-ion/litre?

83. What is the maximum concentration of H^+ at which practically all Zn^{2+} is precipitated with hydrogen sulphide?

84. Calculate the maximum concentration of H^+ in a solution from which practically all Cd^{2+} is to be precipitated.

85. At what hydrogen ion concentration will Fe^{2+} be precipitated with hydrogen sulphide? Is this process feasible?

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* To solve this problem proceed from the assumption that an ion is completely precipitated if its concentration in the solution is less than 10^{-4} g-ion/litre. Precipitation is considered impossible if the concentration of unprecipitated ions exceeds 1 g-ion/litre. Precipitation is feasible at any hydrogen ion concentration if its calculated value exceeds 10 g-ion/litre.

Follow this assumption in solving other problems.

86. At what maximum hydrogen ion concentration can practically all Sn^{2+} be precipitated?

87. At what hydrogen ion concentration can practically all Zn^{2+} be precipitated without involving Ni^{2+} ion?

88. A 0.5*N* solution of acetic acid contains Mn^{2+}, Pb^{2+}, and Cu^{2+} ions. Which of them can be precipitated by saturation with hydrogen sulphide?

89. A 1*N* solution of acetic acid contains Fe^{2+}, Zn^{2+}, and Cd^{2+} ions. Which substances will be precipitated by hydrogen sulphide?

90. 2.0 ml of sulphuric acid (density, 1.80 g/cc) are diluted with a solution containing Fe^{2+}, Cd^{2+}, and Cu^{2+} ions to make 100 ml. Which ions will be precipitated by hydrogen sulphide?

E. Complex compounds

Composite ions, formed by the union of several ions, or of ions and uncharged particles, are known as *complex ions.* For example, as Fe^{3+} combines with CN^- the new ion $[Fe(CN)_6]^{3-}$ is formed, which differs in its properties from the parent ions. Complex compounds are important for their quite specific properties.* When we make out equations for the reactions through which complex compounds are formed, we must remember the rule for determining the charge of a complex ion, viz.: *the charge on a complex ion equals the algebraic sum of the component ion charges.*

Example 1. Determine the charge of a complex ion $[Fe(CN)_6]^x$ in which the oxidation state of iron is +3.

Solution. The charge on the iron ion is +3, while the charge on the six ions of monobasic hydrocyanic acid is —6. The algebraic sum of the charges will be —3:

$$(+3) + (-6) = -3.$$

This is the charge on the complex ion.

Example 2. What is the oxidation state of cobalt in the complex ion $[Co(NO_2)_6]^{3-}$?

* Complex compounds formed by cations with organic compounds are known as *complexones.*

Solution. Designate the oxidation state of cobalt by x. The ion NO_2^- bears the charge —1. Hence:

$$x + (-6) = -3; \text{ whence } x = +3.$$

Example 3. What is the oxidation state of mercury in the complex ion $[Hg(NH_3)_4]^{2+}$?

Solution. Since the NH_3 particles are neutral (their charge is zero) the charge on the mercury ion equals the charge of the whole complex, i.e. +2.

The formation of complex ions can be regarded as a reversible chemical reaction. The solution of a complex compound, along with complex ions, also contains a certain number of ions from which the complex is formed. The complex ions in solution can therefore be regarded as a weak electrolyte obeying the laws of mass action and ionic equilibrium. For example, an equation expressing the reaction leading to dissociation of the complex ion $[Fe(CN)_6]^{3-}$ can be written as the equation of a reversible reaction:

$$[Fe(CN)_6]^{3-} \rightleftharpoons Fe^{3+} + 6CN^-$$

and the law of ionic equilibrium can be applied to it:

$$\frac{[Fe^{3+}]\,[CN^-]^6}{[Fe(CN)_6]^{3-}} = K_{dis.}$$

The dissociation constant of a complex is called the *instability constant.* It characterizes the instability of a given complex: the lower the instability constant, the less readily a complex falls into the parent ions, i.e. the more stable is the complex, while conversely, a high instability constant indicates that the complex is unstable and that its solution contains a large number of the original ions. Double salts can be regarded as complex compounds from this standpoint, because their instability constants are high compared with the usual complex compounds.

To determine the concentration of the initial ion in the solution of a complex compound, it is necessary to work out the equation of the ionic equilibrium for the given complex, to designate the unknown quantities by x, to substitute the value of the instability constant (from Table 7 in the Appendix), to set out the formula for calculation, and to find the

required value. Approximate results will be sufficient for the problems given in this section, and the roots should therefore be found only to the second significant figure. Roots of the 2nd and 3rd power can be found from tables, and of higher powers by using logarithms, assuming that $\log \sqrt[n]{a} = \frac{\log a}{n}$. Before extracting a root, the subradical expression should be so transformed that it becomes a product of a whole number (or a mixed decimal fraction) and 10 raised to the power multiple of the root exponent.

Example 4. Determine the concentration of the ions Hg^{2+} and Cl^- in a 0.1*M* solution of $K_2[HgCl_4]$.

Solution. Since the solution concentration is not high and all salts are well dissociated, assume that the total concentration of the $[HgCl_4]^{2-}$ ion is also 0.1 g-ion/litre. Write down the equation of the complex ion dissociation:

$$[HgCl_4]^{2-} \rightleftharpoons Hg^{2+} + 4Cl^-.$$

Use the formula of the law of ionic equilibrium:

$$\frac{[Hg^{2+}]\,[Cl^-]^4}{[HgCl_4]^{2-}} = 6 \times 10^{-17}.$$

(The value of K is taken from the table.)

Designate $[Hg^{2+}]$ by x. Then $[Cl^-] = 4x$; assume $[HgCl_4]^{2-}$ to be equal to the total concentration of the solution (0.1 g-ion/litre), since the instability constant of this complex is very low. Substitute all data in the formula

$$\frac{x\,(4x)^4}{0.1} = 6 \times 10^{-17}$$

whence $256x^5 = 6 \times 10^{-18}$

and

$$x = \sqrt[5]{\frac{6}{256}\,10^{-18}} = \sqrt[5]{0.0234 \times 10^{-18}} =$$

$$\sqrt[5]{2.34 \times 10^{-20}} \simeq 1.2 \times 10^{-4} \text{ g-ion/litre.}$$

The chloride ion concentration will be four times greater.

$$1.2 \times 10^{-4} \times 4 = 4.8 \times 10^{-4} \text{ g-ion/litre.}$$

Problems

1. Write down the equations of the reactions by which the following substances are formed and dissociated: (a) aluminium ammonium sulphate; (b) potassium ferricyanide.

2. Write down the equations of the reactions by which the following substances are formed and dissociated: (a) Mohr's salt; (b) potassium ferrocyanide.

3. Write down the equations of the reactions by which the following substances are formed and dissociated: (a) (a) ferric ammonium sulphate; (b) ammoniated copper sulphate.

4. Write down the equations of the reactions by which the following substances are formed and dissociated: (a) potassium chloroplatinate; (b) cobaltic thiocyanate.

5. Write the structural formulas of the following: (a) $[Pt(NH_3)_6]Cl_4$; (b) $K_2[Co(CNS)_4]$.

6. Write the structural formulas of the following: (a) potassium ferrocyanide; (b) potassium ferricyanide.

7. Write the structural formula of a compound having the following formula: $PtCl_4 \cdot (NH_3)_6$.

8. Write the empirical and structural formulas of all possible compounds that can be obtained from $[Pt(NH_3)_6]Cl_4$ by replacing ammonia particles in the inner coordination sphere by chloride ions from the outer sphere.

9. What are the coordination numbers of the complexing agents in the following compounds: (a) potassium ferrocyanide; (b) potassium ferricyanide; (c) ammoniated cadmium sulphate?

10. What are the coordination numbers of the complexing agents in the following compounds: (a) potassium chloroplatinate; (b) ammoniated silver chloride; (c) ammoniated copper sulphate?

11. What are the charges on the following complex ions: $[Fe^{2+}(CN)_6]^x$, $[Fe^{3+}(CN)_6]^x$, $[Pt^{4+}(NH_3)_6]^x$, $[Pt^{4+}(NH_3)_2Cl_4]^x$?

12. What are the charges on the following complex ions: $[Ag(NH_3)_2]^x$, $[AgCl_2]^x$, $[AgS_2O_3]^x$?

13. What are the charges on the complexing agents in the following compounds: (a) $H_2[PtCl_6]$; (b) $[Ni(NH_3)_6](OH)_2$; (c) $H_2[HgI_4]$?

14. What are the charges on the complexing agents in the following compounds: (a) $K_3[Co(NO_2)_6]$; (b) $[Ni(NH_3)_4](OH)_2$; (c) $[Ag(NH_3)_2]Cl$?

15. Write down the mathematical expressions of the instability constants for the following complexes:
(a) $[Fe(CN)_6]^{4-}$; (b) $[Hg(NH_3)_4]^{2+}$; (c) $[AgCl_2]^-$.

16. Write out the mathematical expressions of the instability constants for the following complexes:
(a) $[Cd(NH_3)_4]^{2+}$; (b) $[Fe(CN)_6]^{3-}$; (c) $[HgBr_4]^{2-}$.

17. There are two solutions of $K[AgCl_2]$ and of $Na[Ag(CN)_2]$, having the same concentrations and volumes. In which of them is the concentration of the Ag^+ ion greater? How much greater?

18. There are two 0.1*N* solutions, of $[Ag(NH_3)_2]Cl$ and $K[Ag(S_2O_3)]$. In which of them is the concentration of Ag^+ greater?

19. There are two equal volumes of cadmium chloride solution of the same concentration. One of them is treated with excess ammonia and the other with excess potassium cyanide. In which of them is the concentration of Cd^{2+} greater?

20. There are solutions of potassium ferrocyanide and of potassium ferricyanide. In which of them, under equal conditions, is the concentration of the iron ion greater?

21. Determine the concentration of Ag^+ and NH_3 in a 0.1*M* solution of $[Ag(NH_3)_2]OH$.

22. Determine the concentration of Ag^+ and Cl^- ions in a 1*N* solution of $K[AgCl_2]$.

23. There are two equal portions of a 0.1*M* solution of copper sulphate. One of them is treated with excess KCN and the other with excess ammonia. In which of them is the quantity of copper ion greater?

24. How will the cobalt ion concentration change in a 1*M* solution of ammonia on oxidation with the oxygen of the air?

25. Add 5 ml of ammonia solution to 10 ml of a 0.1*N* solution of copper sulphate which has the effect of the copper being completely bound in a complex. What will happen if we pass hydrogen sulphide into the solution?

26. Will any precipitation occur as we pass hydrogen sulphide through a 0.1*N* solution of $K_2[Cd(CN)_4]$?

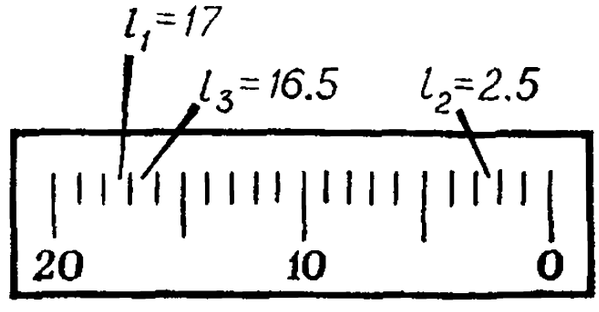
CHAPTER TWO

GRAVIMETRIC ANALYSIS

A. Weighing on a Balance

The main technique upon which quantitative analysis depends is measuring mass. The accurate weighing of substances is done on an analytical balance. The accurate determination of weight starts with the determination of the zero point of a balance.

The zero point of a balance is the reading on the scale from which the pointer of the balance when unloaded deviates to either side through an equal number of scale divisions. The



zero point is found by three consecutive readings of the pointer as it freely swings with no load in the pans. The extreme right division of the scale is assumed to be the zero point, and readings are taken from the right to the left (see the picture), provided the weights are placed in the right-hand pan of the balance. The zero point L_0 is calculated from the Gauss formula

$$L_0 = \frac{l_1 + 2l_2 + l_3}{4}.$$

Example 1. Determine the zero point of a balance using the data given in the figure above.

Solution.

$$\frac{17 + 2 \times 2.5 + 16.5}{4} = 9.6.$$

The equilibrium point of a balance is determined by the same procedure except that the balance is loaded. The coincidence of the balance point with a zero reading of the pointer indicates that the balance (periodic) is set at an equilibrium state.

Using weights gives an accuracy to the measurement of mass of hundredths of a gram. Thousandths and ten-thousandths of a gram are measured by using riders and a rider bar. In order to determine the mass of a body, corresponding to the given position of a rider, its force moment, the product of the rider mass (0.01 g) and the distance from the beam end (zero reading) to the point where the rider rests, is first determined. The distance is expressed in fractions of the beam length, which is assumed to be unity.

Example 2. The rider rests at the second intermediate mark of the scale between the eighth and ninth numbered divisions of the rider bar. What is the mass of the body?

Solution.

$$0.01 \times 0.84 = 0.0084 \text{ g}.$$

The distance between the numbered divisions of the rider bar can be subdivided into five or ten smaller divisions each of which corresponds to two hundredths and one hundredth of the beam length respectively. Each small division corresponds to $0.02 \times 0.01 = 0.0002$ g for the rider bar of the first type and to $0.01 \times 0.01 = 0.0001$ g for the rider bar of the second type.

The sensitivity of a balance is very important for accurate weighing. It is expressed by the number of milligrams that swing the balance pointer one division of the rider bar. The greater this number, the less the sensitivity of the balance.

Example 3. Place a body on the balance pan and equilibrate the balance by weights and a rider set at the 4th division of the scale. The equilibrium point is 8.6. Move the rider to the 6th division; the equilibrium point moves to 14. What is the sensitivity of the balance?

Solution. The movement of the rider from the 4th to the 6th division corresponds to an increase in force of 2 mg, with the result that the equilibrium point shifts to 14 —

— 8.6 = 5.4 divisions. Using the definition of sensitivity work out the proportion and solve it

$$\begin{array}{l} 2 \text{ mg} - 5.4 \text{ divisions} \\ \\ x \text{ mg} - 1 \text{ division} \end{array} \qquad x = \frac{2}{5.4} = 0.37 \text{ mg.}$$

Correct weights are very important for determining mass on precision balances. Errors due to inaccurate weights should not distort the result by more than 0.01 per cent.

Example 4. What is the maximum allowable error of a weight whose nominal mass is 2 g?

Solution.

$$\begin{array}{l} 2 \text{ g} - 100\% \\ \\ x - 0.01\% \end{array} \qquad x = \frac{2 \times 0.01}{100} = 0.0002 \text{ g.}$$

Problems

1. In determining the zero point of a balance three consecutive readings of the pointer were taken: $l_1 = 19.5$, $l_2 = 1.0$, and $l_3 = 19$. What is the zero point of the balance?

2. With the free swinging of the beam of an unloaded balance the pointer reads consecutively: $l_1 = 15$, $l_2 = 4.5$, and $l_3 = 14.5$. Determine the zero point of the balance.

3. During the determination of the zero point of a balance, the following data were obtained: $l_1 = 19.5$, $l_2 = 4.5$, and $l_3 = 18.9$. In what direction, to the right or to the left, should the counterweights be moved on the beam to equilibrate the balance?

4. As the pointer of an unloaded balance swings, it reads the following: $l_1 = 14.5$, $l_2 = 0.5$, and $l_3 = 14$. In what direction should the counterweights be shifted to equilibrate the system?

5. Determine the stability of a balance when a series of readings gave the following results: first series of observations: $l_1 = 17.5$, $l_2 = 2.5$, $l_3 = 17$; second series: $l_1 = 13.5$, $l_2 = 7.0$, $l_3 = 13$. Do the deviations exceed acceptable levels?

6. Are the readings of a balance sufficiently stable if two series of observations are as follows: first series: $l_1 = 18$; $l_2 = 2.0$; $l_3 = 17.5$; second series: $l_1 = 15$; $l_2 = 6.5$; and $l_3 = 14.5$? What is the deviation between the results of the two series?

7. What is the force moment of a rider of normal mass if it is set on the right-hand arm of a beam at the third intermediate notch between the sixth and seventh numbered divisions?

8. A rider of normal mass is set at the second intermediate notch between the fourth and fifth numbered divisions of the left-hand arm of a beam. What is the rider force moment if the body to be weighed is put in the left-hand pan?

9. What is the force moment of a rider set in the middle of a two-sided rider bar of a beam?

10. What is the force moment of a rider placed directly in the right-hand pan of a balance with the body to be weighed placed in the left-hand pan?

11. Will the equilibrium be upset if a rider taken from the tenth division of the right-hand beam arm is put in the right-hand pan?

12. A rider is set at the zero division. What is its force moment?

13. The true mass of a rider is 0.0095 g. What is its force moment, if it is set at the fourth intermediate position between the eighth and ninth numbered divisions?

14. What is the force moment of a rider placed at the first intermediate division between the second and the third numbered divisions, if the true mass of the rider is 11 mg?

15. The zero point of a balance is 9. A rider is set at the second numbered division of the right-hand arm and the following readings are obtained: $l_1 = 19.5$, $l_2 = 11.5$, and $l_3 = 19$. What is the sensitivity of the balance?

16. During the determination of the sensitivity of a balance the following data were obtained: in determining the zero point, $l_1 = 18.0$, $l_2 = 2.5$, and $l_3 = 17.5$; with the rider set at the fifth division of the right-hand arm, $l_1 = 20.0$, $l_2 = 11.7$, and $l_3 = 19.0$. What is the sensitivity of the balance (a) in milligrams per division and (b) in divisions per mg?

17. What is the mass of a body if it can be counterbalanced with 20 g and 1 g weights placed in the right-hand pan of the

balance with the rider set at the sixth division of the rider bar of the left-hand arm of the beam?

18. To counterbalance a body placed in the left-hand pan of a balance, 5 g and 500 mg weights were placed in the right-hand pan and a rider moved to the 3.2 mark on the left-hand arm. What is the mass of the body?

19. A body is placed in the left-hand pan of an equilibrated balance and a 10 g weight in the right-hand pan. A rider is placed at the fourth intermediate notch between the ninth and tenth divisions of the left-hand arm of the beam. What is the mass of the body?

20. To what change in the mass of a body does shifting a rider from the tenth division of the right-hand arm of a beam to the tenth division of the left-hand arm correspond?

21. The zero point of a balance is 9.0. A watch glass is counterbalanced by weights of 5 and 1 g, and 200, 100, and 20 mg in the right-hand pan. The rider is fixed at the fifth division of the right-hand arm of the beam; the equilibrium point then becomes 10.6. After the rider has been shifted to the fourth division of the same arm, the equilibrium point becomes 8.4. Determine the mass of the watch glass to an accuracy of one ten thousandth of a gram.

22. The zero point of a balance is 10.2. Weights (7.2800 g) are placed in the right-hand pan. With the rider set at the sixth division of the right-hand arm, the equilibrium point is 9.5. When the rider is moved to the seventh division of the same arm, the equilibrium point becomes 12. Determine the mass of the body.

23. A crucible has been equilibrated on a balance and its mass determined: 6.8946 g. When the mass of the rider was checked, it proved to be 8.5 mg. What is the actual mass of the crucible if the rider was on the right-hand arm and the crucible in the left-hand pan of the balance?

24. The mass of a body was determined: 12.4968 g. The rider is on the left-hand arm of the beam. What is the mass of the body if the true mass of the rider is 0.0011 g?

25. A crucible was weighed twice. When weighed in the left-hand pan the balance read 12.4556 g and in the right-hand pan, 12.4552 g. What is the mass of the crucible?

26. A weighing bottle was weighed in the left-hand pan of a balance and then in the right-hand one. The results were

31.4812 g and 31.4808 g respectively. What is the true mass of the weighing bottle?

27. The distance between the knife edges of the prisms of an analytical balance is 175.0000 mm. The mass of a body as determined in the left-hand pan is 28.3642 g and in the right-hand one, 28.3636 g. Which of the beam arms is longer?

28. The length of the left-hand arm is 80.0000 mm. How much longer can the right-hand arm be if the error, due to inequality of the beam arms, is not to exceed 0.0002 g when a body with a mass of 5.0000 g is being weighed?

29. The absolute error of 20 g and 0.1 g weights is +0.0002 g. What is the relative error of each weight?

30. What is the absolute error of a 5 g weight if its relative error is 0.01 per cent?

31. The left-hand arm of a balance is slightly longer than the right-hand one. What is the sign of the allowed error if the balance is used without correction for inequality of the beam arms?

32. What is the sign of the error if we use a balance whose right-hand arm is longer than the left-hand one (assume that the body to be weighed is placed as usual in the left-hand pan of the balance)?

33. A weighing bottle containing a sample was placed in the left-hand pan of an aperiodic balance and a weight of 68 g in the right-hand pan. The rider discs read 580 and the scale of the weightograph, +2.8. What is the mass of the weighing bottle containing the sample?

34. A crucible is placed in the left-hand pan of an aperiodic balance, and a weight of 7 g in the right-hand one. The rider discs read 090, and the weightograph scale, +3.2. Determine the mass of the crucible.

35. A watch glass was weighed on an aperiodic balance; the mass of the weights was 10 g, the rider discs read 800, and the weightograph, —0.5. What is the mass of the watch glass?

36. An iron wire was weighed on an aperiodic balance without any weights. The rider discs read 910 and the weightograph, —0.5. What is the mass of the wire?

B. Calculating the mass of a sample

There are three types of gravimetric determinations:

I. The sought component is isolated quantitatively from the sample and weighed.

II. The sought component is removed quantitatively from the sample and the residue weighed.

III. The sought component is converted quantitatively into another chemical compound that can be isolated quantitatively from the sample and weighed.

The method of calculating the mass of a sample depends on the particular type of gravimetric determination. *A sample of a substance is a small (usually* 0.1-1.0 *g) quantity of the substance in question which is accurately weighed and then subject quantitatively to all analytical procedures.* The weight of a sample for the first two types of determination should be such that the isolated or the removed component weighed about 0.01-0.1 g.

The mass of a sample for the third type of analysis must be sufficient to give the following quantities of precipitates (depending on the character of precipitate), in grams:

Amorphous, light (hydroxides)	0.07-0.1
Crystalline, light (most salts)	0.1-0.15
Crystalline, heavy ($BaSO_4$, etc.)	0.2-0.4
Crystalline, very heavy ($PbSO_4$, AgCl, etc.)	up to 0.5

Problems

1. Determine the weight of a sample of peat for testing for moisture, if the expected moisture content is about 15 per cent.

2. Calculate the weight of a sample of coal for testing for volatile substances if their expected content is about 20 per cent.

3. Determine the weight of a coal sample for testing for ash, if its expected content is about 10 per cent.

4. Calculate the weight of a sample of an alloy containing about 56 per cent of gold, if the sought metal is isolated in a free state during the analysis.

5. Determine the weight of a sample of blue vitriol, $CuSO_4 \cdot 5H_2O$, for determining the water of crystallization.

6. Calculate the weight of a sample of sodium carbonate, $Na_2CO_3 \cdot 10H_2O$, for determining water of crystallization.

7. Calculate the weight of a limestone sample for the test for CaO by incineration.

8. Determine the weight of a magnesite sample for the test for CO_2 by incineration, if the sample consists of 90 per cent of $MgCO_3$ and 10 per cent of non-carbonates and non-volatile admixtures.

9. Calculate the weight of a limestone sample for testing for moisture, if the expected moisture content of the sample is about 15 per cent.

10. Calculate the weight of a limestone sample for the test for CO_2, if it contains about 85 per cent of $CaCO_3$.

11. Determine the weight of a chalk sample for the test for CaO, if the sample contains about 20 per cent of moisture.

12. Calculate the weight of a cast iron sample for testing for silicon by dissolution in hydrochloric acid, if the silicon content of the sample is about 2 per cent.

13. Determine the weight of a peat sample for testing for ash, if the ash content of the sample is about 20 per cent.

14. Determine the weight of a chalk sample for the test for insoluble admixtures, if their content in the sample is about 0.3 per cent.

15. Determine the weight of a coal sample containing about 4 per cent of sulphur for the determination of sulphur as $BaSO_4$.

16. Calculate the weight of an iron sulphide sample containing about 30 per cent of sulphur for the determination of sulphur as $BaSO_4$.

17. Determine the weight of a sample of $BaCl_2 \cdot 2H_2O$ for the test for barium, if it is determined as $BaSO_4$.

18. Determine the weight of a sample of $CuSO_4 \cdot 5H_2O$ for the test for copper, if it is determined as CuO after precipitation.

19. A mixture of equal quantities of barium chloride and sodium chloride is to be tested for barium content. What should the weight of the sample of such a mixture be, if barium is precipitated as $BaSO_4$?

20. Determine the weight of a sample of a 30 per cent iron sulphide for testing for sulphur, if it is determined as $BaSO_4$.

21. Determine the weight of a piece of wire containing about 98 per cent of iron for the determination of iron, if the metal is precipitated as $Fe(OH)_3$.

22. Determine the weight of a sample of ore containing about 70 per cent of iron for the determination of iron, if the metal is precipitated as $Fe(OH)_3$.

23. Calculate the weight of a sample of commercial green vitriol containing about 90 per cent of $FeSO_4 \cdot 7H_2O$ for testing for $FeSO_4 \cdot 7H_2O$, if it is precipitated as $Fe(OH)_3$.

24. Determine the weight of a sample of siderite for the determination of iron, if the sample contains about 75 per cent of $FeCO_3$ and the precipitate is $Fe(OH)_3$.

25. Calculate the weight of a sample of limestone containing about 8 per cent of impurities for testing for $CaCO_3$, if it is precipitated as $CaC_2O_4 \cdot H_2O$.

26. Calculate the weight of a calcite sample for the determination of calcium, if calcium is precipitated as $CaC_2O_4 \cdot H_2O$ and the initial calcite contains virtually no impurities.

27. Calculate the weight of a marble sample for the determination of CaO.

28. A sample of slaked lime contains about 15 per cent of impurities. What should the weight be of its sample for the determination of Ca as CaO?

29. Calculate the weight of a sample of an alloy containing about 0.5 per cent of magnesium for the determination of magnesium, if the precipitate is $NH_4MgPO_4 \cdot 6H_2O$.

30. Determine the weight of a sample of an alloy containing about 95 per cent of magnesium for the determination of magnesium, if the precipitate is $NH_4MgPO_4 \cdot 6H_2O$.

31. Determine the weight of a sample of dolomite containing about 10 per cent of magnesium for the test for MgO, if magnesium is precipitated as $NH_4MgPO_4 \cdot 6H_2O$.

32. Determine the weight of a sample of dolomite containing about 20 per cent of MgO for testing for magnesium, if it is precipitated as $NH_4MgPO_4 \cdot 6H_2O$.

33. Calculate the weight of a sample of zinc sulphate for the determination of zinc, if the metal is precipitated as $NH_4ZnPO_4 \cdot 6H_2O$.

34. Determine the weight of a sample of commercial magnesium sulphate (heptahydrate) containing about 5 per cent of impurities for the test for purity.

35. Calculate the weight of a sample of sodium metaphosphate for the determination of phosphorus, if it is precipitated as $NH_4MgPO_4 \cdot 6H_2O$.

36. Calculate the weight of a sample of phosphorite containing about 15 per cent of P_2O_5 for the determination of phosphorus, if it is determined as magnesium pyrophosphate and precipitated as $NH_4MgPO_4 \cdot 6H_2O$.

37. Determine the weight of a sample of aluminium potassium sulphate for the determination of aluminium, if it is precipitated as $Al(OH)_3$.

38. Calculate the weight of a sample of feldspar for the test for Al_2O_3, if its content of the sample is about 8 per cent.

39. Calculate the weight of a sample of commercial NaCl containing about 6 per cent of impurities for the determination of chlorine as AgCl.

40. Determine the weight of a sample of barium chloride for the determination of chlorine as AgCl.

41. Calculate the weight of a sample of an alloy containing about 85 per cent of silver for the determination of silver, if it is precipitated and determined as chloride.

42. Determine the weight of a sample of silver nitrate for the determination of silver, if it is precipitated and determined as AgCl.

43. Should the weights of samples of $CaCl_2 \cdot 6H_2O$ be equal if we test them for calcium as CaO and for chlorine as AgCl?

44. Should the weights of barium chloride samples be equal if we test them for (a) barium and (b) chlorine?

45. Determine the weights of samples of an alloy containing about 72 per cent of gold, 22 per cent of silver, and 6 per cent of copper for the test for all these components, if silver is determined as AgCl, copper as CuO, and gold as pure metal.

46. Calculate the weight of a siderite sample for the determination of Fe as Fe_2O_3, if the $FeCO_3$ content of the sample is 70 per cent.

47. Use reference tables to find the composition of alloys and weighing forms in which the alloy components are determined, and calculate the weight of tombac samples for the determination of all constituents of the alloy.

48. Do the same for silumin.

49. Do the same for Devarda's metal,

50. Do the same for brass.

C. Calculating the amounts of solvent and precipitating agent

The quantities of solvent to dissolve the sample and also of a precipitating agent should be calculated to the second degree of accuracy. In other words, these calculations are approximate, and only one or two significant figures remain in the final results. The theoretical basis for such calculations is the law of equivalent weights: *all substances combine with one another in quantities proportional to their equivalent weights.* Hence the proportion:

$$\frac{E_{\text{solute}} - E_{\text{solv}}}{m - x}$$

where E_{solute} is the equivalent weight of the solute or substance to be precipitated; E_{solv} is the equivalent weight of the solvent or precipitating agent; m is the mass of the solute or precipitated substance contained in the sample; and x is the mass of the solvent or precipitating agent.

If the concentration of the reagent used in the analysis is other than 100 per cent, designated as a %, the sought weight quantity of the reagent, in grams, will be:

$$m' = \frac{x \times 100}{a}$$

In order to convert units of mass into units of volume, the found quantity m' should be divided by the density of the solution. Since these calculations are approximate, the density of dilute solutions should be assumed to be unity. Finally, in order to ensure a complete reaction, the found quantity should be multiplied several times in accordance with the following rule: *if a solvent (or a precipitating agent) is a volatile substance, it should be taken in quantities two or three times greater than the quantity calculated by using equivalent weights; the quantity of non-volatile substances should exceed the calculated amount by* 1.5 *times.*

If the concentration of a reagent is expressed in g-equiv/lit the following proportion should be worked out:

$$\frac{\begin{array}{l}E_{\text{solute}} \text{ — 1000 ml of a } 1N \text{ solution of the solvent} \\ \qquad\qquad \text{(precipitating agent)} \\ m \text{ g — } x \text{ ml of a } 1N \text{ solution of the solvent} \\ \qquad\qquad \text{(precipitating agent)}\end{array}}{}$$

If the concentration of the reagent is other than 1*N*, the found volume should be changed in the inverse proportion to its concentration. For example, if it is found that a 1*N* solution should be taken in the quantity x ml, then a 2*N* solution should be taken in the quantity $\frac{x}{2}$, and a 0.5*N* solution in the quantity $\frac{x}{0.5} = 2x$ ml.

Problems

Note: If the amount of reagent excess is not specified, the results of the solution can differ significantly from the answers given in the end of the textbook.

1. How many millilitres of 1*N* HCl, with a 100 per cent excess, are required to dissolve 1 g of chalk?
2. How many millilitres of 1*N* HNO_3, with a 50 per cent excess, are required to dissolve about 2 g of calcite?
3. What volume, in ml, of 1.5*N* HCl, with a 200 per cent excess, is required to dissolve about 0.2 g of iron?
4. What volume, in ml, of 4*N* HCl, with a 100 per cent excess, is required to dissolve 0.1 g of an iron wire?
5. What volume, in ml, of 4*N* H_2SO_4, with a 100 per cent excess, is required to dissolve 0.1 g of magnesium carbonate containing 90 per cent of $MgCO_3$?
6. What volume, in ml, of 2*N* NaOH, with a 100 per cent excess, is required to dissolve about 0.5 g of commercial aluminium?
7. What volume, in ml, of 0.5*N* HCl is required to dissolve 1.5 g of chalk containing about 25 per cent of moisture and insoluble impurities?
8. What volume, in ml, of 0.1*N* H_2SO_4 is required to dissolve 1 g of magnesite containing 10 per cent of insoluble impurities?
9. What volume, in ml, of a solution containing 200 g of H_2SO_4 in 1 litre should be taken to dissolve about 0.5 g of zinc?
10. What volume, in ml, of a solution containing 54 g of HCl in 1 litre should be taken to dissolve 5 g of calcite?
11. What volume, in ml, of a 10 per cent solution of H_2SO_4 is required to dissolve 0.2 g of iron containing 10 per cent of insoluble impurities?

12. What volume, in ml, of a 15 per cent solution of HCl is required to dissolve 1.5 g of magnesium oxide?

13. What volume, in ml, of an H_2SO_4 solution (density, 1.102 g/cc) is required to dissolve 0.3 g of magnesium?

14. What volume, in ml, of a 10 per cent solution of H_2SO_4 is required to dissolve 0.3 g of aluminium?

15. What volume, in ml, of HCl (density, 1.057 g/cc), taken in excess, is required to dissolve 1 g of dolomite, $CaCO_3 \cdot MgCO_3$?

16. What volume, in ml, of ammonia solution (density, 0.958 g/cc) is required to dissolve 0.3 g of copper oxide?

17. What volume, in ml, of HCl (density, 1.018 g/cc) is required to dissolve 2.5 g of slaked lime containing about 10 per cent of insoluble impurities?

18. A solution contains 50 g of HCl in 1 litre. What volume, in ml, of this solution is required to dissolve 2 g of quick lime containing 25 per cent of moisture and insoluble impurities?

19. What volume, in ml, of potassium hydroxide solutio (density, 1.14 g/cc), with a 200 per cent excess, is required to dissolve 0.2 g of an aluminium wire?

20. What volume, in ml, of ammonia solution (density, 0.994 g/cc), with a 50 per cent excess, is required to dissolve 0.4 g of AgCl containing 30 per cent of insoluble impurities?

21. What volume, in ml, of 1*N* HCl, with the excess as required, is needed to precipitate Ag^+ from a solution obtained by the dissolution of 1 g of silver?

22. What volume, in ml, of a 2*N* solution of ammonia is required to precipitate Fe^{3+} from a solution containing 0.2 g of iron?

23. What volume, in ml, of 2*N* H_2SO_4, with the excess as required, is needed to precipitate barium from a solution containing 0.6 g of $BaCl_2 \cdot 2H_2O$?

24. What volume, in ml, of a 1*N* solution of H_2SO_4 is required to precipitate barium from a solution obtained by the dissolution of 0.9 g of barium chloride containing 40 per cent of impurities?

25. What volume, in ml, of a 4*N* solution of Na_2HPO_4 is required to precipitate magnesium from a solution obtained by the dissolution of 0.4 g of an alloy containing 60 per cent of magnesium?

26. What volume, in ml, of a 0.2*N* solution of $H_2C_2O_4$ is required to precipitate calcium from a solution obtained by dissolving 0.6 g of marble?

27. What volume, in ml, of 0.5*N* $(NH_4)_2C_2O_4 \cdot H_2O$ is required to precipitate quantitatively calcium from a solution prepared from 1 g of chalk containing 25 per cent of moisture and insoluble impurities?

28. What quantity, in grams, of $Na_2HPO_4 \cdot 12H_2O$ is required to precipitate quantitatively magnesium from a solution obtained by the dissolution of 1.5 g of dolomite?

29. What quantity, in grams, of $H_2C_2O_4 \cdot 2H_2O$ is required to precipitate quantitatively calcium from 50 ml of a solution obtained by dissolving 1 g of marble in 250 ml of solvent?

30. What quantity, in grams, of $(NH_4)_2HPO_4$ is required to precipitate magnesium from a solution obtained by dissolving 0.8 g of dolomite?

31. What volume, in ml, of a 2*N* solution of $BaCl_2$ is required to precipitate SO_4^{2-} from 2 g of commercial concentrated sulphuric acid?

32. What volume, in ml, of a 0.5*N* solution of barium chloride is required to precipitate barium as $BaSO_4$ from a solution obtained by the appropriate treatment of 1.5 g of coal containing about 2 per cent of sulphur?

33. What volume, in ml, of a 10 per cent solution of ammonia is required to precipitate 0.15 g of iron?

34. What volume, in ml, of a 5 per cent ammonia solution is required to precipitate iron from a solution obtained by dissolving 0.3 g of hematite containing about 10 per cent of rock?

35. What volume, in ml, of a 10 per cent ammonia solution is required to precipitate iron from a solution prepared by the dissolution of 0.4 g of magnetite?

36. What volume, in ml, of a 7 per cent solution of $Na_2HPO_4 \cdot 12H_2O$ is required to precipitate magnesium from a solution of 0.4 g of $MgSO_4 \cdot 7H_2O$ (assume the density of the solution to be unity)?

37. What volume, in ml, of ammonia solution (density, 0.960 g/cc) is required to precipitate iron from a solution of 0.5 g of Mohr's salt, if its Fe^{2+} is preliminarily oxidized to Fe^{3+}?

38. What quantity, in ml, of ammonia solution (density, 0.980 g/cc) is required to precipitate quantitatively iron from a solution prepared by dissolving 0.2 g of siderite containing 30 per cent of iron?

39. What quantity, in ml, of a solution of HCl (density, 1.028 g/cc) is required to precipitate silver from a solution obtained by dissolving 1.5 g of an alloy containing 10 per cent of silver?

40. Dissolve 2 g of barite containing 20 per cent of impurities, and add water to make 250 ml. What volume, in ml, of H_2SO_4 (density, 1.032 g/cc) is required to precipitate barium from 50 ml of the prepared solution?

41. Dissolve 2 g of asbestos containing about 1 per cent of aluminium and iron in a 250-ml volumetric flask and add water to the mark. What volume, in ml, of 0.1*N* ammonia solution is required to precipitate sesquioxides from 25 ml of the obtained solution?

42. Dissolve 2 g of an alloy containing about 70 per cent of silver in a volumetric flask and add water to 500 ml. What volume, in ml, of HCl (density, 1.018 g/cc) is required to precipitate silver from 25 ml of the solution?

43. Calculate the weight of an iron wire and the quantities of the reagents required for testing for iron. Use the reagents in concentrations of your own choice.

44. Proceed as instructed in the previous problem to determine CaO in quick lime containing 15 per cent of moisture.

45. Proceed as instructed in Problem 43 to determine barium in a mixture of salts containing about 40 per cent of barium.

46. Proceed as instructed in Problem 43 to determine silver in an alloy containing about 60 per cent of silver.

47. Proceed as instructed in Problem 43 to determine calcium in chalk containing about 10 per cent of moisture and 15 per cent of insoluble impurities.

48. Proceed as instructed in Problem 43 to determine magnesium in dolomite containing insignificant quantities of impurities.

49. Proceed as instructed in Problem 43 to determine aluminium as Al_2O_3 in aluminium bronze.

50. Proceed as instructed in Problem 43 to determine aluminium in duralumin.

D. Calculating the loss in precipitate washing

In order to calculate the loss occurring during the washing of precipitates, it is necessary first to determine the solubility product of the substance to be precipitated (from reference tables) and then (from the solubility product) the ion concentration in the washings, which turn into a saturated solution on contact with the precipitate. Next the number of grams of the precipitated substance in 1 litre of its saturated solution is found, and finally the total number of grams of the substance contained in the entire volume of the washings. Since the loss of the precipitate during washing with pure water can be significant, the loss is reduced by adding to the washing water the ion which is contained in the precipitate but is not to be determined in the analysis. For example, when barium is determined as $BaSO_4$, small quantities of sulphuric acid are added to the washing water.

Example. A precipitate of $BaSO_4$ weighing 0.2 g is washed with 150 ml of liquid prepared from 1 litre of water and 0.5 ml of a $4N$ solution of sulphuric acid. What percentage of the precipitate has passed into the solution?

Solution. Determine the concentration of H_2SO_4 in the washing liquid. For H_2SO_4 $4N$ is $2M$. When 0.5 ml of this solution is mixed with 1 litre of water, its concentration decreases

$$\frac{1000}{0.5} = 2000 \text{ times, or to } [H_2SO_4] = [SO_4^{2-}] =$$

$$= \frac{2 \times 0.5}{1000} = 0.001 = 10^{-3} \text{ mole/litre.}$$

Using the rule of the solubility product, determine the concentration of Ba^{2+} and the equivalent concentration of $BaSO_4$ in the saturated solution. The SP of $BaSO_4$ is $[Ba^{2+}]\,[SO_4^{2-}] \approx \approx 1 \times 10^{-10}$. Set out and solve the equation where $[Ba^{2+}]$ is designated by x, and substituting the found quantity for $[SO_4^{2-}]$:

$$x\,[SO_4^{2-}] = 1 \times 10^{-10} \text{ or } x\,10^{-3} = 1 \times 10^{-10};$$

$$x = 10^{-7} \text{ g-ion/litre.}$$

The same number of moles of $BaSO_4$ is contained in one litre.

Finally, determine the quantity of $BaSO_4$ contained in 150 ml of the saturated solution, expressing the result in per cent of the weight of the washed precipitate:

$$\frac{1 \times 10^{-7} \times 233 \times 150 \times 100}{1000 \times 0.2} \approx 2 \times 10^{-3} = 0.002 \text{ per cent.}$$

Problems

1. Wash $BaSO_4$ precipitate with 250 ml of distilled water. Calculate the number of grams of the precipitate that has passed into solution.
2. Wash $CaC_2O_4 \cdot H_2O$ precipitate with 500 ml of distilled water. Calculate the number of grams by which the mass of the precipitate diminished.
3. What quantity, in grams, of $BaCrO_4$ precipitate will pass into solution if it is washed with 300 ml of distilled water?
4. What quantity, in grams, of $CaSO_4$ precipitate will pass into solution if it is washed with 100 ml of distilled water?
5. Wash $Mg(OH)_2$ precipitate with 500 ml of distilled water. What quantity, in grams, of Mg^{2+} ion has passed into solution.
6. Wash NH_4MgPO_4 precipitate with 350 ml of distilled water. What quantity, in grams, of magnesium has passed into solution?
7. Wash 0.1 g of $BaSO_4$ precipitate with 250 ml of pure water. What quantity, in per cent, of the precipitate has passed into solution?
8. Wash 0.15 g of $BaCO_3$ precipitate with 200 ml of distilled water. Determine the loss, in per cent, of the precipitate due to dissolution.
9. Calculate the quantity, in per cent, of the precipitate that has passed into solution on washing 0.1 g of $CaC_2O_4 \cdot H_2O$ with 150 ml of distilled water.
10. Determine the loss, in per cent, of 2 g of $CaSO_4$ precipitate when it is washed with 100 ml of distilled water.
11. Determine the loss, in per cent, of $NH_4MgPO_4 \cdot 6H_2O$ if 0.05 g of it is washed with 200 ml of distilled water.
12. What quantity, in per cent, of $BaCrO_4$ has passed into solution if 0.01 g of it is washed with 100 ml of distilled water?

13. Calculate the loss, in per cent, of $CaC_2O_4 \cdot H_2O$ if 0.5 g of it is washed with 200 ml of distilled water.

14. The sulphur content of a sample of coal is 2 per cent. What is the relative error if $BaSO_4$ precipitate obtained from 1.5 g of the sample is washed with 150 ml of distilled water?

15. What quantity, in grams, of $BaSO_4$ will pass into solution if it is washed with 500 ml of a 0.01*M* solution of sulphuric acid?

16. What quantity, in grams, of $BaSO_4$ will dissolve in 250 ml of washing liquid prepared from 500 ml of water and 2 ml of a 0.1*N* solution of sulphuric acid?

17. What quantity, in grams, of $CaC_2O_4 \cdot H_2O$ will pass into solution if it is washed with 100 ml of liquid prepared from 750 ml of water in which 2.13 g of $(NH_4)_2C_2O_4 \cdot H_2O$ have been dissolved?

18. What quantity, in grams, of $SrCO_3$ will pass into solution if it is washed with 250 ml of liquid prepared from 500 ml of water and 5.3 g of anhydrous soda?

19. What quantity, in per cent, of the weight of the precipitate is dissolved if 0.2 g of barium sulphate is washed with 150 ml of liquid prepared from 1 litre of water and 1 ml of 2*N* H_2SO_4?

20. What quantity, in per cent, of the precipitate has passed into solution if 1.5 g of $NH_4MgPO_4 \cdot 6H_2O$ is washed with 250 ml of the liquid prepared from 500 ml of water and 1 ml of a 10 per cent ammonia solution?

21. How many times is the solubility of $BaSO_4$ in distilled water greater than in a washing liquid prepared from 200 ml of water and a drop (about 0.04 ml) of concentrated sulphuric acid?

22. What quantity, in ml, of a 1*M* solution of sulphuric acid should be added to 1 litre of water so that the loss due to the dissolution of $BaSO_4$ (0.1 g) washed with 250 ml of the obtained liquid will not exceed 0.01 per cent?

E. Calculating the gravimetric factor

The gravimetric factor is the ratio of the equivalent weight of the sought component to the equivalent weight of its weighing form. When calculating the gravimetric factor, the ratio of the masses of the corresponding quantities of

molecules (or atoms) of the sought component and its weighing form is usually determined. For example, in order to calculate the gravimetric factor for the determination of Ba as $BaSO_4$, the atomic mass of barium is divided by the molecular mass of its weighing form $BaSO_4$:

$$F_{Ba/BaSO_4} = \frac{Ba}{BaSO_4}.$$

But when calculating the gravimetric factor for the determination of aluminium by its weighing form Al_2O_3, the doubled atomic mass of aluminium should be divided by the molecular mass of Al_2O_3, i.e. $F_{2Al/Al_2O_3} = \frac{2Al}{Al_2O_3}$

The factors and their logarithms are given in Table 2 in the Appendix. Using this table simplifies calculations, saves time, and minimizes possible arithmetic errors (see page 100).

Problems

1. Calculate gravimetric factors for the determination of Ba, BaO, $Ba(OH)_2$, $BaCl_2 \cdot 2H_2O$ by $BaSO_4$. Find their logarithms.
2. Calculate gravimetric factors for the determination of S, H_2SO_4, Na_2SO_4 by $BaSO_4$. Find their logarithms.
3. Calculate gravimetric factors for the determination of Fe, FeO, $FeCO_3$, $(NH_4)_2Fe(SO_4)_2$, $FeCl_3$ by Fe_2O_3. Find their logarithms.
4. Calculate gravimetric factors for the determination of Ca, $CaCO_3$, $CaCl_2$, CO_2 by CaO. Find their logarithms.
5. Calculate gravimetric factors for the determination of P, P_2O_5, $Ca_3(PO_4)_2$, Mg by $Mg_2P_2O_7$. Find their logarithms.
6. Calculate gravimetric factors for the determination of Al, $Al_2(SO_4)_3$, $KAl(SO_4)_2 \cdot 12H_2O$, $AlCl_3$ as Al_2O_3. Find their logarithms.
7. Calculate gravimetric factors for the determination of Pb, PbO, $PbCl_2$, Pb_3O_4 by $PbSO_4$. Find their logarithms.
8. Calculate gravimetric factors for the determination of F as (a) CaF_2, (b) SiF_4. Find their logarithms.
9. Calculate gravimetric factors for the determination of Cu and $CuFeS_2$ as (a) CuO and (b) Cu_2S.

10. Calculate gravimetric factors for the determination of hydrogen as H_2O and carbon as C_2H_2.

11. Calculate the gravimetric factor for the determination of hydrogen fluoride, if during the analysis CaF_2 precipitate is obtained and then dissolved, precipitated with SO_4^{2-}, and weighed as $CaSO_4$.

12. To determine potassium, it can be converted into potassium chloroplatinate, K_2PtCl_6, and then the free platinum, isolated from this compound, is weighed. What is the gravimetric factor?

13. To determine calcium carbide in the commercial product it can be decomposed by water, the liberated acetylene precipitated quantitatively with silver as silver acetylide, and the latter is then converted into AgCl and weighed. What is the gravimetric factor?

14. To determine arsenic, it can be precipitated with hydrogen sulphide as As_2S_3, its sulphur oxidized to the SO_4^{2-} ion, and the ion can then be precipitated with a barium salt and weighed as $BaSO_4$. What is the gravimetric factor?

F. Calculating the results of gravimetric analysis

Calculating the results of gravimetric determinations is the simplest operation in analytical chemistry. If a particular analysis belongs to the first or second type of gravimetric determinations (see page 86), calculation of the results consists in determining the percentage of the sought substance to the weight of the entire sample. In the third type of gravimetric determinations the mass of the sought component is first found:

$$\frac{E_{\text{s. c.}} - E_{\text{w. f.}}}{m_{\text{s. c.}} - m_{\text{p.}}}$$

where $E_{\text{s.c.}}$ is the equivalent weight of the sought component, $E_{\text{w.f.}}$ is the equivalent weight of the weighing form, $m_{\text{s.c.}}$ is the mass of the sought component, and $m_{\text{p.}}$ is the mass of the precipitate.

As a rule, the ratio of equivalent weights is replaced by the ratio of masses of the corresponding number of mole-

cules of the sought component and the weighing form. Once the mass of the sought component has been determined, it is necessary to calculate what percentage it is of the mass of the entire sample. Thus the calculation of the results of all gravimetric analyses relating to the third type can be expressed by the formula

$$x\,\% = \frac{E_{\text{s.c}} \cdot m_{\text{p.}} \cdot 100}{E_{\text{w.f.}} \cdot \text{sample}} = F\,\frac{m_{\text{p.}} \cdot 100}{\text{sample}}.$$

Hence, in order to determine the result of an analysis of the third type, multiply the gravimetric factor (from Table 2) by the mass of the precipitate multiplied by 100, and then divide by the mass of the sample.

Perform all calculations using only tables of logarithms or a calculator.

Problems

1. A sample of an alloy containing copper weighs 0.2152 g. Pure copper, in a quantity of 0.0898 g, is isolated from the sample by electrolysis. Determine the percentage of copper.

2. A sample of dolomite weighs 1.0842 g. The sample is dissolved in an acid, the undissolved precipitate separated on a filter, washed, calcined, and weighed. Its mass is 0.0356 g. Calculate the percentage of insoluble substances in the sample.

3. A sample of an alloy containing gold and weighing 0.1000 g was dissolved in nitric acid. The undissolved gold was separated, washed and calcined. Its mass is 0.0724 g. Calculate the percentage of gold in the sample.

4. A coal sample weighing 2.6248 g was dried to constant mass of 2.5420 g. Calculate the percentage of moisture in the sample.

5. The mass of a dry coal sample was 2.0500 g and after calcining 1.2348 g. Calculate the percentage of volatile substances in the sample.

6. A sample of dry limestone weighs 1.5120 g, while after calcining to constant weight its mass is 0.8470 g. Calculate the CaO and CO_2 percentages in the sample.

7. A sample of peat weighs 1.6340 g. After calcining to constant mass its mass is reduced to 0.4102 g. What is the ash content of the sample?

8. A sample of crystalline sodium carbonate weighing 2.1080 g was partly aired to lose its water of crystallization. The weight of the anhydrous soda is 1.2640 g. Calculate the anhydrous soda percentage in the sample.

9. A sample of coke in a weighing bottle has a mass of 12.6100 g, while the weight of the empty bottle is 10.5650 g After drying to constant mass the bottle containing the sample weighs 12.3750 g. Calculate the percentage of absolutely dry substance in the sample.

10. Water of crystallization was determined in a sample of barium chloride. The data obtained are as follows: the mass of the weighing bottle, 25.6874 g; the mass of the weighing bottle with the sample, 27.2594 g; the same after drying, 27.0269 g. Calculate the percentage of water of crystallization in the sample.

11. The following data were obtained in the determination of hygroscopic water in a sample of sodium chloride: the mass of a crucible, 7.2393 g; the mass of the crucible containing the sample, 7.8809 g; the same after drying, 7.8616 g. Calculate the percentage of hygroscopic water in the sample.

12. The data obtained during the determination of volatile matter in coal are as follows: the mass of a crucible is 5.3280 g; the mass of the crucible containing the sample is 6.5110 g; the mass of the crucible containing the sample after removal of the volatile matter is 6.2745 g. Calculate the percentage of volatile matter in the sample.

13. The results of the analysis of clay are as follows: the mass of a crucible is 20.3650 g; the mass of the crucible containing clay is 21.3870 g; the same after drying to constant weight, at 105°C, is 21.3671 g; the same after ignition is 21.3368 g. Calculate, in per cent: (a) hygroscopic water content of the sample; (b) loss on ignition.

14. A sample of magnesite weighing 0.5062 g is dried at 105°C to constant mass of 0.5043 g. The dry sample is calcined to 0.2512 g. Calculate, in per cent: (a) hygroscopic water content, (b) CO_2 content.

15. A mineral sample weighing 0.5260 g is dissolved, the

insoluble residue separated, washed, and ignited in a crucible. The mass of the crucible containing the residue is 6.7280 g. The residue is treated with H_2F_2 and ignited again. All SiO_2 is thus removed as SiF_4. The mass of the crucible with the new residue is 6.3140 g. Calculate the SiO_2 percentage of the sample.

16. The following results are obtained in the determination of silica (by the procedure described in Problem 15) in cast iron: the mass of the sample, 2.1630 g; the mass of the crucible containing a calcined residue after dissolution of the sample, 5.3396 g; the mass of the crucible with the residue after removal of SiO_2, 5.2930 g. Calculate the percentage of silica in the sample.

17. A sample of limestone is placed in a weighed calcimeter loaded with nitric acid. The mass of the calcimeter without the sample is 78.4564 g; the mass of the apparatus with the sample of limestone is 79.5076 g. The mass of the apparatus after termination of the reaction and quantitative removal of CO_2 is 79.0882 g. Calculate the percentage of CO_2 in the sample.

18. When the CO_2 content of a marble sample was determined by the procedure described in Problem 17, the following results were obtained: the mass of a loaded calcimeter before the introduction of the sample, 65.3462 g; the mass of the apparatus containing the sample, 66.2614 g; the mass of the calcimeter after removal of CO_2, 65.9000 g. Calculate the percentage of CO_2 in the sample.

19. Determine the barium content in 0.4765 g of $BaSO_4$.

20. Determine the sulphur content in 0.2854 g of $BaSO_4$.

21. Determine the silver content in 0.3652 g of AgCl.

22. Determine the chlorine content in 0.3652 g of AgCl.

23. A sample of litharge yields 1.2730 g of $PbCrO_4$ precipitate. What is the lead content of the sample?

24. A sample of magnesite yields 0.2164 g of $Mg_2P_2O_7$ precipitate. Calculate the magnesium content, in grams, of the sample.

25. A sample of a zinc salt yields 0.2587 g of $Zn_2P_2O_7$ precipitate. To what quantities of (a) Zn; (b) ZnO; and (c) $ZnSO_4 \cdot 7H_2O$ does this precipitate correspond?

26. A sample of a ferrous salt gave 0.1652 g of ignited ferric oxide. How many grams of (a) Fe; (b) $FeSO_4$; (c) $FeSO_4 \cdot 7H_2O$ were contained in the sample?

27. A sample of phosphorite gave $Mg_2P_2O_7$ precipitate in a quantity of 0.1829 g. To what quantity of (a) P; (b) P_2O_5; and (c) $Ca_3(PO_4)_2$ does this precipitate correspond?

28. A sample of a potassium salt gave 0.1120 g of K_2PtCl_6 precipitate. To what quantity of (a) K; (b) K_2O; and (c) K_2SO_4 does this precipitate correspond?

29. What quantity, in grams, of AgCl will be obtained from 1.0000 g of pure potassium chloride?

30. What quantity, in grams, of $Mg_2P_2O_7$ will be obtained from 1.3204 g of pure $MgCO_3$?

31. A sample of barium chloride weighing 0.6878 g gave 0.6556 g of $BaSO_4$ precipitate. Calculate the barium content of the sample in per cent.

32. A sample of coal weighing 1.0150 g was treated to give 0.2895 g of ignited $BaSO_4$. Calculate the sulphur content of the sample in per cent.

33. A sample of sulphuric acid weighing 0.3212 g was treated. After precipitation and ignition it gave 0.2642 g of $BaSO_4$ precipitate. What is the percent concentration of the sample?

34. A sample of pyrite weighing 0.2794 g was treated to give 0.4524 g of a calcined precipitate of $BaSO_4$. Calculate the sulphur content of the sample in per cent.

35. A sample of an alloy weighing 0.1000 g gave 0.1196 g of AgCl precipitate. Calculate the silver content of the sample in per cent.

36. A sample of commercial Mohr's salt weighing 0.5012 g is dissolved and precipitated with excess ammonia. The washed precipitate of ferric hydroxide is ignited to constant mass and weighed. The mass of Fe_2O_3 is 0.0968 g. Calculate the percent content of $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ in the sample.

37. A sample of marble weighing 1.8710 gave the following precipitates: 0.0827 g of $Mg_2P_2O_7$, 0.0342 g of Fe_2O_3, and 1.9650 g of $CaSO_4$. Calculate the percentage of Mg, Ca, and Fe in the sample.

38. A sample of an aluminium alloy gave 0.0984 g of Al_2O_3 precipitate. Calculate the aluminium content of the alloy if the sample weight was 0.4524 g.

39. A sample of brass weighing 0.6500 g gave 0.5200 g of $ZnNH_4PO_4$ and 0.0030 g of $PbSO_4$ precipitates. Calculate the zinc, lead, and copper contents of the sample provided it contains no other components.

40. A sample of limestone weighing 0.5210 g gave 0.2218 g of CaO and 0.0146 g of $Mg_2P_2O_7$ precipitates. Calculate the $CaCO_3$ and $MgCO_3$ contents of the sample.

41. A sample of magnesite weighing 2.4110 g gave 2.1710 g of calcined $Mg_2P_2O_7$ precipitate. Determine the content of (a) Mg; (b) MgO; (c) $MgCO_3$ in the sample.

42. A sample of superphosphate weighing 1.4010 g gave 0.1932 g of calcined CaO precipitate. To what percent content of (a) Ca and (b) $Ca_3(PO_4)_2$ does this precipitate correspond?

43. Calculate the $Al_2(SO_4)_3$ content, in per cent, of a sample of commercial aluminium sulphate if 0.5278 g of it gave 0.1552 g of Al_2O_3 precipitate.

44. A sample of commercial aluminium ammonium sulphate weighing 0.8563 g gave 0.0914 g of Al_2O_3 precipitate. Calculate the pure crystal hydrate content of the sample in per cent.

45. A cryolite sample weighing 0.5872 g gave 0.1060 g of Al_2O_3 precipitate. Calculate the Na_3AlF_6 content of the sample in per cent.

46. A sample of potassium aluminium sulphate weighing 0.4000 g was dissolved in water and precipitated with a barium salt. The precipitate was washed with water, ignited, and weighed. Its mass is 0.3880 g. Calculate the $KAl(SO_4)_2 \cdot 12H_2O$ content of the sample.

47. A sample of hematite was dissolved, the iron precipitated with ammonia, and the precipitate calcined to give 0.5390 g of Fe_2O_3. What is the content of Fe and Fe_2O_3 in the sample if its initial weight was 0.6582 g?

48. A sample of $FeCO_3$ was dissolved, oxidized, precipitated, and calcined to give 1.0000 g of Fe_2O_3. Calculate the percentage of Fe and FeO in the sample if its initial weight was 1.5200 g.

49. A sample of magnetite weighing 0.6012 g was treated to give 0.4520 g of Fe_2O_3 precipitate. Calculate the Fe_3O_4 and Fe contents of the sample.

50. A sample of iron, with mass equal to the gravimetric factor for calculating Fe_2O_3 as Fe, expressed in grams, gave

1.0000 g of Fe_2O_3. Did the initial sample contain impurities or was it pure?

51. When barium was determined in a sample of $BaCl_2 \cdot 2H_2O$, the following results were obtained: the mass of the watch glass containing the sample is 12.3762 g; the mass of the emptied glass, 11.6720 g; the mass of the calcined crucible, 9.2738 g; and the mass of the same crucible with the calcined precipitate of $BaSO_4$, 9.9464 g. Calculate the barium content of the sample.

52. The following data were obtained during the analysis of commercial barium chloride: the mass of the weighing box containing the sample, 24.9418 g; the mass of the weighing box less the sample, 24.2982 g; the mass of the empty crucible, 6.2638 g; the mass of the crucible containing the calcined $BaSO_4$ precipitate, 6.7376 g. Calculate the $BaCl_2 \cdot 2H_2O$ content of the sample.

53. The following data were obtained during the analysis of a limestone sample: the mass of the watch glass containing the sample, 9.3310 g; the mass of the emptied glass, 8.6436 g; the mass of the empty crucible, 5.8140 g; the mass of the crucible with the calcined precipitate of CaO, 6.1192 g. Calculate the $CaCO_3$ content of the sample.

54. The following results were obtained during the analysis of a marble sample: the mass of the watch glass containing the sample, 15.2858 g; the mass of the watch glass without the sample, 14.4714 g; the mass of the empty crucible, 5.9428 g; the mass of the crucible containing the precipitate after the precipitation of calcium with ammonium oxalate and calcined to constant mass, 6.3326 g. Calculate the percentage of impurities that do not contain calcium.

55. The following data were obtained during the analysis of a sample of dolomite: the mass of the watch glass with the sample, 5.6102 g; the mass of the glass less the sample, 5.2132 g; the mass of the crucible with the precipitate after the precipitation of magnesium with ammonium hydrophosphate, calcined to constant mass, 6.2846 g; the mass of the empty crucible, 6.1224 g. Calculate the MgO content of the sample.

56. The following results were obtained during the analysis of carbonate rock: the mass of the watch glass containing the sample, 12.8116 g; the mass of the glass less the sam-

ple, 12.4236 g; the solution, obtained by dissolving the sample, is separated from an insoluble residue and sesquioxides and treated with ammonium oxalate; the mass of the calcined precipitate together with the crucible is 7.2444 g; the mass of the empty crucible is 7.1242 g. Calculate the Ca content of the sample.

57. After nitrogen was determined gravimetrically in an organic compound it was converted into NH_4^+ and precipitated with chloroplatinic acid. The precipitate was calcined to complete decomposition and weighed. Calculate the nitrogen content of the compound if its sample weighed 0.1012 g and the mass of the calcined precipitate was 0.0572 g.

58. After ammonia was determined in a sample of an organic fertilizer (see Problem 57) weighing 0.1128 g, a precipitate was obtained. Its weight was 0.0984 g. Calculate the NH_3 content of the sample.

59. A sample of commercial cadmium sulphate weighing 0.3006 g was treated to give 0.1986 g of $Cd_2P_2O_7$ precipitate. Calculate the cadmium content of the sample.

60. A sample of chamber acid weighing 17.0200 g was tested for HNO_3. After the nitron treatment it gave 0.0908 g of $C_{20}H_{16}N_4 \cdot HNO_3$ precipitate. What is the HNO_3 content of the sample?

61. A sample of a sodium salt was dissolved and precipitated with magnesium uranyl acetate. The yield of the anhydrous precipitate $NaMg(UO_2)_3(CH_3COO)_9$ was 0.9980 g. What is the content, in grams, of sodium in the sample?

62. A sample of nickel silver weighing 1.2014 g was tested for nickel, which was precipitated with dimethylglyoxime. The mass of the dried precipitate of nickel dimethylglyoxime is 0.7990 g. Calculate the nickel content of the alloy.

63. During the analysis of commercial $NiSO_4 \cdot 7H_2O$, 0.2842 g of nickel dimethylglyoxime was obtained. Calculate the percentage of the main substance in the sample if it weighed 0.2988 g.

64. A sample of bone meal weighing 0.1562 g was treated to give 0.4980 g of $(NH_4)_3PO_4 \cdot 12MoO_3$. Calculate the percentage of P_2O_5 in the sample.

65. A sample of manganine weighing 5.1128 g was tested for nickel. After treatment and precipitation with dimethyl-

glyoxime, the precipitate was washed and calcined. The mass of precipitate thus treated was 0.1998 g. Calculate the percentage of nickel in the sample.

66. A sample of double superphosphate weighing 0.5238 g was treated with magnesia mixture, and the precipitate was washed and calcined. The mass of the precipitate is 0.3840 g. Calculate (a) the phosphorus and (b) P_2O_5 contents of the sample.

67. A sample of dolomite weighing 0.9980 g was dissolved and aluminium precipitated from it as hydroxyquinolate. The mass of the washed and dried precipitate was 0.1000 g. Calculate the percentage of aluminium in the sample.

68. A sample of dolomite weighing 0.3996 g gave the following precipitates: 0.1234 g of CaO and 0.1836 g of $Mg_2P_2O_7$. What is the percentage of (a) $CaCO_3$ and (b) $MgCO_3$ in the sample?

69. A sample of limestone weighing 1.2300 g was dissolved in acid, the solution filtered and treated with ammonium hydroxide. The mass of the calcined precipitate of sesquioxides was 0.0584 g. Aluminium was isolated from the precipitate as Al_2O_3. The mass of the weighing form after ignition was 0.0232 g. What is the percentage of (a) Fe and (b) Al in the sample?

70. A sample of calcite weighing 0.4180 g gave 0.2342 g of calcined CaO precipitate. Did the initial calcite contain impurities or was it pure calcium carbonate?

71. A sample of calcium carbonate weighing 1.7847 g gave 0.5603 g of calcined CaO precipitate. Calculate the percent content of $CaCO_3$ in the sample.

72. Calculate the weight of a sample for testing for calcium carbonate if we want the percentage of $CaCO_3$ to be equal to the mass of the calcined CaO precipitate multiplied by 100.

73. Determine the mass of the sample for testing for magnesium if we want the mass of the calcined $Mg_2P_2O_7$ precipitate multiplied by 100 to be equal to the percentage of magnesium in the sample.

74. Calculate the mass of a sample for testing for phosphorus if we want the percentage of phosphorus in the sample to be equal to the mass of the calcined precipitate of $Mg_2P_2O_7$ multiplied by 100.

75. Hydrogen is determined in an organic compound by the mass of water obtained during combustion of the substance. What should the mass of the sample be if we want the percentage of hydrogen to be equal to the mass of the water obtained multiplied by 10?

76. Calculate the mass of a sample of phosphorite if we want the mass of $P_2O_5 \cdot 24MoO_3$ subsequently formed multiplied by 10 to be equal to the percentage of phosphorus in the sample.

77. What is the content of the sought component in a sample if the mass of the weighing form obtained in the course of the analysis is 1 g or its decimal fraction?

78. What is the weight of a dried silver chloride precipitate which is obtained from a sample of a silver alloy weighing 0.1000 g, if the Ag content is 90.00 per cent?

79. What will be the mass of a calcined $BaSO_4$ precipitate obtained by processing 1.5000 g of coal, if it contains 5.00 per cent of sulphur?

80. A sample of limestone containing 43.32 per cent of CaO gave 1.3000 g of a calcined $CaSO_4$ precipitate. Determine the initial weight of the sample.

81. A sample of potassium aluminium sulphate containing 97.61 per cent of $KAl(SO_4)_2 \cdot 12H_2O$ gave 0.2584 g of $BaSO_4$. What was the initial weight of the sample?

82. A sample of apatite containing 14.74 per cent of phosphorus gave 0.9926 g of $(NH_4)_3PO_4 \cdot 12MoO_3$. What was the original weight of the sample?

83. A mixture of pure potassium chloride and sodium chloride, containing certain amounts of hygroscopic water, weighs 0.1150 g. The mixture gives 0.2645 g of AgCl and 0.0326 g of K_2PtCl_6. Calculate the percentage of NaCl.

84. A sample of crystalline zinc sulphate, weighing 1.2500 g, was tested for K_2SO_4 (impurity). The sample gave 0.8128 g of $BaSO_4$ and 0.5298 g of $Zn_2P_2O_7$. What is the K_2SO_4 content of the sample?

85. A sample of pure $BaCl_2 \cdot 2H_2O$ gave 0.1820 g of $BaSO_4$ precipitate. What is the mass of the AgCl precipitate obtained from the same sample?

86. A sample of pure $CaCO_3$ was calcined to constant weight. The calcined precipitate weighs 0.1124 g. What quantity of CO_2, in grams, was liberated?

87. A sample of $CaCl_2 \cdot 6H_2O$ gave 0.2020 g of CaO. What quantity, in grams, of AgCl will be obtained from the same sample?

88. A sample of commercial aluminium sulphate is free from impurities containing Al^{3+} or SO_4^{2-} ions. What would the mass of a calcined precipitate of Al_2O_3 be if the sample gave 0.4264 g of $BaSO_4$?

89. A sample of iron sulphate crystal hydrate gave 0.1132 g of Fe_2O_3 and 0.3309 g of $BaSO_4$ precipitates. Can sulphates of other metals or iron salts of other acids be present among the impurities?

90. An equimolecular mixture of potassium chloride and sodium chloride is prepared. Two equal samples gave 0.2880 g of K_2PtCl_6 and 0.3396 g of AgCl. Is the composition of the mixture correct? If not, then which component prevails in the mixture?

91. A sample of crystalline magnesium sulphate gave 0.2748 g of $BaSO_4$ and 0.1280 g of $Mg_2P_2O_7$. What are the impurities in the sample: sulphates of elements other than magnesium or magnesium salts of acids other than sulphuric? The sample contains no other ions giving these weighing forms.

92. A sample of $CaCO_3$ can contain calcium salts of acids other than carbonic, or carbonates of elements other than calcium. Which of these possible impurities is present in the sample if it gave 0.1846 g of CaO and 0.1658 g of CO_2?

93. A preparation of sodium sulphate is re-crystallized and kept in the air. A sample weighing 0.7872 g gave 0.5108 g of calcined $BaSO_4$ precipitate. Calculate the moisture content of the preparation. Has it partly lost or gained moisture from the air on standing?

94. A sample of pure potassium chloride and sodium chloride weighing 0.2584 g gave 0.5408 g of K_2PtCl_6 precipitate. What is the NaCl content of the mixture?

95. A mixture of pure $CaCO_3$, $MgCO_3$, and NaCl weighing 0.9334 g gave 0.1602 g of CaO and 0.6459 g of $Mg_2P_2O_7$. Calculate the percentage of NaCl in the mixture.

96. A sample of pure crystalline borax weighing 1.2190 g gave 0.4451 g of B_2O_3. Calculate the content of water of crystallization in the sample.

97. A sample of a mineral weighing 0.8864 g gave 0.1038 g of sesquioxide precipitate. After dissolution it was established

that the precipitate contained 28.50 per cent of Al_2O_3. Calculate the content of (a) Al and (b) Fe in the sample.

98. A preparation of magnesium nitrate contains sodium chloride and sodium bromide as impurities. A sample weighing 1.1260 g was dissolved and treated with silver nitrate solution. The obtained precipitate, weighing 0.0980 g, contained 65.80 per cent of AgCl. Determine the NaBr content of the sample.

99. A sample of zinc ore weighing 0.5232 g was treated to give 0.7850 g of zinc pyrophosphate. Cadmium was anticipated in the precipitate. The precipitate was dissolved, cadmium detected and removed, while zinc converted into the sulphide and weighed. Its mass was 0.4954 g. Calculate the percentage of cadmium in the sample (as CdS).

100. A sample of lead ore weighing 0.4864 g gave 0.4732 g of sulphides (precipitate). After the second dissolution of the precipitate and re-precipitation of the solution obtained with hydrochloric acid, 0.0124 g of AgCl precipitate was obtained (the ore contained small quantities of silver). Calculate the percentage of lead in the sample if other metals precipitated with hydrogen sulphide in an acid medium were not detected.

G. Calculations involving the removal or introduction of a component

If a given component is determined in a moist sample (a), and the sample is then dried and the component determined again, the new result (c) will be greater than the former by the number of times 100 is greater than the difference ($100 - b$), where b is the moisture content of the sample, in per cent. This equation can be expressed by the following formula

$$c = \frac{a \times 100}{(100 - b)}.$$

Example 1. The ash content of a moist peat sample is 21 per cent. What is the ash content of a dried sample if its moisture content is 30 per cent?

Solution.

$$c = \frac{21 \times 100}{(100-30)} = 30 \text{ per cent.}$$

The ash content of a moist peat sample is, on the contrary, less than the ash content of a dry sample:

$$a = \frac{c\,(100-b)}{100}.$$

Example 2. The ash content of a dry peat sample is 20 per cent. What is the ash content of the sample before drying if it contains 30 per cent of moisture?

Solution.

$$a = \frac{20\,(100-30)}{100} = 14 \text{ per cent.}$$

In the ultimate analysis of all substances, determinations are usually done with air-dried samples. The moisture content is determined in a special sample and the results are recalculated for an absolutely dry substance. The sum of all results of the ultimate analysis (analytical balance) should be equal to 100 per cent. This is essential evidence of correctness of the analysis.

Problems

1. The CaO content of chalk containing 8.00 per cent of moisture is 50.50 per cent. Calculate the percentage of CaO in an absolutely dry sample.
2. A sample of ore having 7.12 per cent of moisture contains 20.54 per cent of iron. What is the iron content of an absolutely dry sample?
3. A sample of coal contains 8.95 per cent of ash and 6.25 per cent of moisture. Calculate the percentage of ash in an absolutely dry sample.
4. An air-dry sample of limestone contains 39.07 per cent of calcium. After calcining its weight reduced from 0.9234 g to 0.5263 g. Determine the percent content of calcium in the calcined product.
5. A sample of lime has the following composition, in per cent: CaO, 85.84; MgO, 10.45; (Al_2O_3 + Fe_2O_3), 0.97;

SiO_2, 0.79; (H_2O + CO_2), 1.98. Determine the composition of the sample calculating as the absolutely dry calcined matter.

6. A sample of clay has the following composition, in per cent: SiO_2, 44.90; Al_2O_3, 39.32; H_2O, 9.48; Fe_2O_3, 0.65; CaO, 0.55; MgO, 0.38; TiO_2, 0.82; the rest, 3.90. Calculate the composition of the sample with reference to an absolutely dry substance.

7. The following data (in per cent) were obtained in the analysis of a dolomite sample: CO_2, 46.66; MgO, 22.07; CaO, 30.59; sesquioxides, 0.56; insoluble residue, 0.37; moisture, 0.19. What is the composition of the calcined residue?

8. The following results, in per cent, were obtained in the analysis of a carbonate rock: CO_2, 46.80; MgO, 21.24; CaO, 30.77; sesquioxides, 0.22; insoluble residue, 0.46; moisture, 0.13. Calculate the results of the analysis for an absolutely dry substance.

9. A sample of barium chloride weighing 1.0070 g was dried to constant mass of 0.8586 g. A sample of the original substance weighing 0.7042 g was calcined to give 0.6727 g of $BaSO_4$ precipitate, while another sample weighing 0.2468 g gave 0.2896 g of AgCl precipitate. Calculate the percent composition of the original substance and recalculate as a dehydrated substance.

10. A sample of ferriammonium sulphate weighing 0.9644 g gave 0.9337 g of $BaSO_4$ and 0.1597 g of Fe_2O_3 precipitates. Determine the percentage of Fe^{3+} and SO_4^{2-} ions in the sample and recalculate it as a dry substance, assuming that a molecule of the alum contains twelve molecules of water of crystallization.

11. A sample of pyrite weighing 1.7890 g was dried to 1.7180 g. A sample of the same original substance, weighing 0.3980 g, gave a calcined precipitate of $BaSO_4$ weighing 1.0780 g. Determine the percentage of sulphur of the original sample and recalculate it as an absolutely dry substance.

12. A sample of commercial blue vitriol weighing 0.5964 g was dried to 0.3748 g. A sample of the original substance, weighing 2.1100 g, gave 0.6350 g of CuO. Determine the percentage of copper in the sample and recalculate it as an anhydrous substance.

13. The following results were obtained during the analysis of an absolutely dry sample, in per cent: CaO, 76.14; MgO, 18.52; SiO_2, 4.00, and CO_2, 1.37. A sample of the same substance, before removal of moisture, weighed 1.0380 g, and after drying at 105°C, 0.9178 g. Determine the percent composition of the original product.

14. The following results were obtained during the analysis of a sample of dolomite dried to constant weight, in per cent: CO_2, 40.49; CaO, 56.60; sesquioxides, 2.17; SiO_2, 0.74. A sample of the substance before drying weighed 0.9844 g, and after calcining to constant mass, 0.5181 g. Determine the percent composition of the original substance.

15. A sample of coal weighing 1.9982 g is treated to remove volatile matter and moisture. Its new weight is 1.2612 g. The ash content of the coke thus prepared is 11.32 per cent. What is the ash content of the original sample?

16. A sample of coal contains 8.12 per cent of moisture and 24.05 per cent of volatile matter. During the coking process a sample weighing 1.3875 g gave 0.2080 g of ash. Calculate the ash content of the original coal sample.

17. A partly calcined sample of lime contains the following, in per cent: CaO, 76.14; MgO, 10.40; SiO_2, 4.00; sesquioxides, 1.37; ($CO_2 + H_2O$), 8.12. What is the composition of the same sample if its moisture is removed completely and the CO_2 content decreased to 0.5 per cent?

18. Anhydrous ferric sulphate contains 39.93 per cent of Fe_2O_3 and 60.07 per cent of SO_3. What is the composition of the crystal hydrate containing nine molecules of water of crystallization?

19. A sample of coal contains 4 per cent of moisture and 8 per cent of ash. What is the ash content of the same sample if its moisture content increased to 12 per cent?

20. The price of peat containing 10 per cent of moisture is 2.40 rubles per ton. What is the price of the same peat if its moisture content increases to 20 per cent, assuming that the price rises with decreasing moisture content?

H. Deriving formulas of substances

The object of the chemical analysis of substances is to determine their chemical formulas. In some cases it is sufficient to establish the number of atoms of each element in

the molecule of a substance. For example, if it is established that the molecule of a given substance contains three atoms of Ca, two atoms of P, and eight atoms of O, the formula of the substance is then $Ca_3(PO_4)_2$. In some cases it is useful to represent the formula of a substance as a combination of oxides, e.g. $Al_2O_3 \cdot 3SO_3$. Finally, the composition of a substance is often expressed as a combination of several molecules of simpler composition (double salts) and crystal hydrates).

Such problems are solved in two steps. First the ratio of the number of particles (atoms, ions, simple molecules) contained in the molecule of a given substance is determined from the following formula:

$$\frac{a}{A} : \frac{b}{B} : \frac{c}{C} = x : y : z,$$

where A, B, C are the atomic (or molecular) masses of particles making up the molecule; a, b, c are their percentages in the test substance; and x, y, z are the number of particles in the molecule of the simplest composition.

The ratio thus obtained, expressed in fractions, should be converted into a ratio of whole numbers.

Example 1. The analysis of a substance is, in per cent: Bi, 59.19; S, 13.62; O, 27.19. What is the simplest formula of the substance?

Solution.

$$\frac{59.19}{209} : \frac{13.62}{32.064} : \frac{27.19}{16} = 0.2832 : 0.4248 : 1.6994 = x : y : z.$$

Assume the smallest number to be unity and divide the other two by it to find:

$$x : y : z = 1 : 1.5 : 6.$$

A molecule cannot contain a fractional number of particles and all terms should therefore be doubled:

$$x : y : z = 2 : 3 : 12,$$

i.e. a molecule of the substance contains two Bi atoms, three S atoms, and 12 O atoms. The formula of the substance is $Bi_2(SO_4)_3$.

Isomorphism is often observed in many naturally occurring chemical compounds. This means that a chemical element in a compound can be partly substituted for some other element which is similar to it with respect to valency and other properties. For example, magnesium is substituted for varying amounts of calcium in natural limestones, with the result that their chemical composition differs depending on the particular deposit. In order to indicate isomorphic substitution, the composition of limestone is expressed by the formula $(Ca,Mg)CO_3$. Formulas of such compounds cannot be established directly, since the ratio $x : y : z$ will not be a ratio of whole numbers in this case, this being the sign of isomorphic substitution. If however we want to express the ratio of all terms by whole numbers, we have to sum up those terms which represent isomorphically substituted elements.

Example 2. The analysis of a mineral is as follows, in per cent: Ca, 9.20; Mg, 22.0; C, 13.7; O, 55.1 Derive the simplest formula of the mineral.

Solution.

$$\frac{9.2}{40.08} : \frac{22.0}{24.31} : \frac{13.7}{12.01} : \frac{55.1}{16} = \overbrace{0.23 : 0.91}^{1.14} : 1.14 : 3.44 = 1 : 1 : 3$$

The formula of the compound is $(Ca,Mg)CO_3$.

Problems

Note: Problems in this section should be solved as accurately as possible.

1. What is the chemical formula of a substance having the following composition: Ca, 71.47 per cent and O, 28.53 per cent?

2. A substance contains 63.52 per cent Fe and 36.48 per cent S. What is its chemical formula?

3. A substance contains 42.88 per cent C and 57.12 per cent O. What is its chemical formula?

4. What is the chemical formula of a compound if it contains 75.26 per cent Ag and 24.74 per cent Cl?

5. What is the chemical formula of a compound containing 84.98 per cent Hg and 15.02 per cent Cl?

6. A chemical substance has a molecular mass of 135.04 and consists of 47.49 per cent S and 52.51 per cent Cl. Determine its chemical formula.

7. What is the chemical formula of a compound consisting of 62.53 per cent Ca and 37.47 per cent C?

8. The analysis of a pyrite sample shows that it consists of 53.45 per cent S and 46.55 per cent Fe. What is the chemical formula of the mineral?

9. What is the chemical formula of a fluoride if it consists of 51.33 per cent Ca and 48.67 per cent F?

10. Pyrolusite contains 63.19 per cent Mn and 36.81 per cent O. What is the chemical formula of the mineral?

11. A mineral consists of 56.03 per cent CaO and 43.97 per cent CO_2. What is its chemical formula?

12. A substance consists of 36.23 per cent MgO and 63.77 per cent P_2O_5. What is the chemical formula of the substance?

13. Corundum consists of 52.92 per cent Al and 47.08 per cent O. Determine its chemical formula.

14. Stibnite consists of 71.68 per cent Sb and 28.32 per cent S. Determine its chemical formula.

15. Copper sulphate crystal hydrate consists of 63.92 per cent $CuSO_4$ and 36.08 per cent H_2O. What is the chemical formula of the crystal hydrate?

16. Zinc sulphate consists of 56.14 per cent $ZnSO_4$ and 43.86 per cent H_2O. What is the formula of the crystal hydrate?

17. Mirabilite contains 44.09 per cent Na_2SO_4 and 55.91 per cent H_2O. What is the chemical formula of the mineral?

18. Carnallite consists of 26.83 per cent KCl, 34.24 per cent $MgCl_2$, and 38.91 per cent H_2O. What is the chemical formula of this mineral?

19. Cryolite consists of 32.85 per cent Na, 12.85 per cent Al, and 54.30 per cent F. What is its chemical formula?

20. What chemical formula corresponds to the composition of bornite (purple copper ore) if it consists of 63.31 per cent Cu, 11.13 per cent Fe, and 25.56 per cent S?

21. Apatite consists of 39.74 per cent Ca, 18.43 per cent P, 3.77 per cent F, and 38.07 per cent O. What is the chemical formula of the mineral?

22. Determine the chemical formula of a mineral consisting of 24.95 per cent Fe, 46.46 per cent Cr, and 28.59 per cent O.

23. Wollastonite consists basically of 34.50 per cent Ca, 24.18 per cent Si, and 41.32 per cent O. What is the chemical formula of wollastonite?

24. Rhodonite has basically the following composition, in per cent: Mn, 41.93; Si, 21.43; O, 36.63. Determine its chemical formula.

25. One of the pyrrhotites consists of 60.38 per cent Fe and 39.62 per cent S. Determine its chemical formula.

26. A zeolite, known as natrolite, consists of 12.09 per cent Na, 14.19 per cent Al, 22.16 per cent Si, 42.08 per cent O and 9.48 per cent readily removable water. What is the formula of the mineral?

27. Phosphorite consists of 39.13 per cent Ca, 1.95 per cent F, 3.28 per cent Cl, and 55.63 per cent PO_4^{3-}. What chemical formula represents this composition?

28. Determine the chemical formula of wolframite if it is known to consist of 6.71 per cent Fe, 11.53 per cent Mn, 60.66 per cent W, and 21.10 per cent O.

29. Derive the chemical formula of a mineral consisting of 20.65 per cent Al_2O_3, 7.03 per cent Fe_2O_3, 27.65 per cent CaO, and 44.55 per cent SiO_2.

30. The composition of a mineral is as follows, in per cent: MnO, 46.36; CaO, 6.91; SiO_2, 46.83. What is its chemical formula?

I. Indirect determinations

All the cases of analytical calculation given above involve solving a mathematical equation with only one unknown quantity. But in some cases not all the required data for solving an equation are available. Here more complicated calculations are involved, using systems of equations with several (usually two) unknowns. This is an indirect method of analysis. Consider a few examples.

Example 1. It has been established that the CO_2 content of a mixture of pure $MgCO_3$ and $BaCO_3$ is 43.97 per cent. Calculate the percentage of each component in the mixture.

Solution. Let the given mixture contain a % of $MgCO_3$ and b % of $BaCO_3$. The first equation is then

$$a + b = 100. \qquad (1)$$

Next we determine the CO_2 content of the pure mixture components:

$$\frac{CO_2 \times 100}{MgCO_3} = 52.19 \text{ per cent (for } MgCO_3)$$

and

$$\frac{CO_2 \times 100}{BaCO_3} = 22.30 \text{ per cent (for } BaCO_3)$$

(The formulas of the substances stand for their molecular masses.)

The content of CO_2 in each component of the mixture is:

$$\frac{a \times 52.19}{100} \% \quad \text{(for } MgCO_3)$$

and

$$\frac{b \times 22.30}{100} \% \quad \text{(for } BaCO_3)$$

The total content of CO_2 in the mixture is 43.97 per cent (stated in the problem). Hence

$$\frac{a \times 52.19}{100} + \frac{b \times 22.30}{100} = 43.97 \text{ per cent}$$

$$0.5219a + 0.2230b = 43.97 \text{ per cent.} \qquad (2)$$

Thus we have a simultaneous equation with two unknowns. Solve it to find:

$a = 72.50$ per cent, and $b = 27.50$ per cent.

Example 2. A sample of a mixture of NaCl and NaBr weighing 0.1809 g is treated with $AgNO_3$ solution to give 0.3715 g of precipitate. Calculate the content of NaCl and NaBr in the mixture.

Solution. Designate the quantities of NaCl and NaBr in the mixture as x and y respectively. Then

$$x + y = 0.1809. \qquad (1)$$

During precipitation, each molecule of NaCl forms a molecule of AgCl and each NaBr molecule forms AgBr. Hence x g of NaCl form

$$\frac{x\ \text{AgCl}}{\text{NaCl}} = \frac{x \times 143.32}{58.44} = 2.4524x \text{ g of AgCl},$$

while y g of NaBr give

$$\frac{y\ \text{AgBr}}{\text{NaBr}} = \frac{y \times 187.78}{102.90} = 1.8249y \text{ g of AgBr}.$$

Use these data to work out the second equation:

$$2.4524x + 1.8249y = 0.3715. \qquad (2)$$

Solve the simultaneous equation to find:

$$x = 0.0660 \text{ g} \quad \text{and} \quad y = 0.1149 \text{ g}.$$

Finally, determine the percentages of the components:

$$\frac{0.0660 \times 100}{0.1809} = 36.48\%\ \text{NaCl}; \quad \frac{0.1149 \times 100}{0.1809} = 63.52\%\ \text{NaBr}.$$

The results obtained by the indirect method are less reliable, and this method should only be used if direct calculations are impossible. The smallest errors in determining the mass (of the sample or the precipitate), the contamination of the precipitates, a small difference in the atomic weights of the main sought elements, and errors in rounding the results, all reduce the reliability of indirect calculations.

Problems

1. An unknown substance was identified as $SrCO_3$ by analysing for CO_2 content. But qualitative analysis showed the absence of Sr^{2+} ion and the presence of Ca^{2+} and Ba^{2+} ions. What is the true composition of the substance in question?

2. The bromine content of a sample is equal to the bromine content of NaBr. What is the true composition of the sample if it contains cations of only ammonium and potassium?

3. A mixture of KCl and KI weighing 0.2120 g gave 0.1994 g of K_2SO_4. What is the content, in grams, of KCl and KI in the sample?

4. A mixture of NaCl and NaBr weighing 0.1798 g is treated with $AgNO_3$ to give 0.3802 g of precipitate. What quantities, in grams, of each component are contained in the sample?

5. A mixture of NaCl and KCl weighing 0.2905 g gave 0.3502 g of a mixture of sodium sulphate and potassium sulphate. Calculate the content of NaCl and KCl in the mixture.

6. A mixture of NaCl and NaBr, weighing 0.3988 g, was precipitated quantitatively with $AgNO_3$ to give 0.7822 g of precipitate. Determine the composition of the mixture.

7. A sample of a mixture of $CaCO_3$ and $MgCO_3$ weighing 0.8210 g was calcined to give 0.4306 g of calcium oxide and magnesium oxide. Determine the percentage composition of the mixture.

8. A sample of dolomite, weighing 0.1840 g, was treated to give 0.0915 g of calcium oxide and magnesium oxide. Calculate the contents of CaO and MgO in the sample.

9. A sample of sylvinite weighing 1.4260 g gave a dry residue of KCl and NaCl weighing 1.1410 g. The residue was converted into sulphates with a mass of 1.3547 g. Calculate the contents of KCl and NaCl in the sample.

10. Potassium and sodium were isolated quantitatively as a solution of chlorides, with a volume of 200.0 ml from a sample of silicate weighing 1.3345 g. A portion of the chloride solution measuring 50.00 ml gave 0.2052 g of AgCl precipitate. Calculate the contents of K_2O and Na_2O in the sample if the mass of potassium chloride and sodium chloride, isolated from a quarter of the sample, is 0.0879 g.

CHAPTER THREE

FUNDAMENTAL THEORY OF TITRIMETRIC (VOLUMETRIC) ANALYSIS

A. Calculations in Titrimetric Analysis

As in gravimetric analysis, so in titrimetric analysis calculations are based on the law of equivalent weights, except that here concentrations and volumes of the reactants are involved. The concentrations of solutions in titrimetric determinations are expressed only in gram-equivalents per litre (normality), and the volumes of solutions, in litres or millilitres. In cases where the quantity of a substance in solution is to be determined, we assume that 1000 ml of a $1N$ standard solution contains 1 g-equiv of the sought substance. And where it is necessary to determine the concentration of a solution, we proceed from the basic principle of titrimetric analysis, that *the volumes of two solutions of the quantitatively reacting substances are inversely proportional to their normalities.*

$$V_1/V_2 = N_2/N_1$$

where V_1 and N_1 are the volume and normality of one of the solutions and V_2 and N_2, of the other.

Problems

1. A sample weighing 0.5080 g was tested for the H_2SO_4 content in solution. The treatment of the test solution, in which 50 ml of $0.2N$ solution of $BaCl_2$ were used up, gave 1.1670 g of $BaSO_4$ precipitate. Calculate the percentage of H_2SO_4 in the sample: (a) from the mass of the obtained precipitate, (b) from the volume of barium chloride solution used up in the analysis.

2. A sample of commercial potassium chloride weighing 0.7142 g was tested for chlorine content. The volume of a

1*N* $AgNO_3$ solution spent for precipitation of Cl^- as AgCl is 10 ml, while the mass of AgCl formed in the reaction is 1.4334 g. Calculate the percentage of chlorine in the sample: (a) from the mass of AgCl precipitate; (b) from the volume and concentration of the $AgNO_3$ solution used up in the analysis.

3. To neutralize a solution of KOH, 25 ml of a 0.1*N* HCl solution were spent. Calculate the quantity, in grams, of KOH contained in the original solution.

4. To neutralize H_2SO_4 solution, 20.50 ml of a 0.2*N* KOH solution were added. Calculate the quantity, in grams, of H_2SO_4 in the solution.

5. Calculate the quantity, in grams, of NaOH contained in a solution, if 22.50 ml of a 0.5*N* HCl solution were spent to neutralize it.

6. Calculate the quantity, in grams, of H_2SO_4 contained in a solution, if 15.50 ml of a 0.3*N* KOH solution are required to neutralize it.

7. How many millilitres of a 0.1*N* HCl solution are required to neutralize a solution containing 1.00 g of NaOH?

8. How many millilitres of a 2*N* NaOH solution are required to neutralize a solution containing 4.9 g of H_2SO_4?

9. To a solution containing 0.5 g of KOH added were 10 ml of a 1*N* solution of H_2SO_4. What substance remained in excess after the reaction? In what quantity?

10. To a solution containing 1.00 g of H_2SO_4 added were 10 ml of a 2*N* solution of NaOH. What is the medium of the resultant solution? What substance remains in excess, and in what quantity?

11. If 20 ml of a 1*N* HCl solution were spent to neutralize a solution containing 1.0 g of caustic soda, calculate the percentage of NaOH in the sample.

12. If 10 ml of a 2*N* NaOH solution were used to neutralize a sample of commercial sulphuric acid weighing 1.00 g, calculate the percentage of H_2SO_4 in the sample.

13. To 25 ml of hydrochloric acid of unknown concentration added are 25 ml of a 0.1*N* NaOH solution. The resultant solution reacts neutral. What is the normality of the original hydrochloric acid?

14. Equal volumes of KOH solution of unknown concentration and a 0.2*N* solution of HCl are mixed together.

What is the normality of the KOH solution if the resultant solution reacts neutral?

15. If 50 ml of H_2SO_4 solution of unknown concentration react quantitatively with 45.65 ml of a 0.1*N* NaOH solution, what is the normality of the H_2SO_4 solution?

16. If 20.50 ml of a 0.2*N* HCl solution were used to neutralize 25 ml of KOH solution, what is the normality of the KOH solution?

17. If 25 ml of a solution react quantitatively with 20 ml of another solution, how do their normalities relate?

18. If 20.00 ml of NaCl solution react quantitatively with 15.00 ml of $AgNO_3$ solution, how do their normalities compare?

19. If 28.50 ml of an acid were used to neutralize 25 ml of an alkali solution, which normality is greater, and by how much?

20. If 25.00 ml of KOH solution were used to neutralize 24.75 ml of HCl solution, the concentration of which solution is higher and how much higher?

21. What volume of a 0.2*N* HCl solution is required to neutralize 40 ml of a 0.1 *N* NaOH solution?

22. What volume of a 0.1*N* $AgNO_3$ is required to precipitate the Cl^- ion quantitatively from 25 ml of a 0.15*N* NaCl solution?

23. If 28.50 ml of KOH solution of unknown concentration were used to neutralize 25.00 ml of a 0.1125*N* solution of H_2SO_4, what is the normality of the solution?

24. If 22.60 ml of a 0.0965*N* solution of HCl were used to neutralize 25.00 ml of NaOH solution, determine the normality of the NaOH solution.

25. If 20.00 ml of KCl solution of unknown concentration react quantitatively with 22.45 ml of a 0.20*N* solution of $AgNO_3$, determine the normality of the KCl solution.

26. If 18.25 ml of a 0.10*N* solution of $KMnO_4$ react quantitatively with 15.00 ml of $FeSO_4$ solution, what is the normality of the latter?

27. What quantity, in ml, of a solution containing 3.646 g of HCl in one litre is required to neutralize 25 ml of a solution containing 4.00 g of NaOH in one litre?

28. What quantity, in ml, of $AgNO_3$ solution containing 17 g of $AgNO_3$ in one litre is required to precipitate quanti-

tatively the chloride ion from 20 ml of hydrochloric acid solution containing 73 g of HCl in one litre?

29. If 10.00 ml of a 25 per cent solution of H_2SO_4 were added to 10.00 ml of a 25 per cent solution of KOH, how does the resultant solution react?

30. Equal volumes of 20 per cent solutions of KOH and HCl are mixed together. What is the medium of the resultant solution?

B. Measuring Volumes

The unit of volume used in the metric system is the volume occupied by the mass of one kilogram of water at its temperature of maximum density ($+3.98°C \cong +4°C$) and atmospheric pressure of 760 mm Hg. This unit is known in volumetric analysis as true litre. In other words, *a true litre is the volume occupied by one kilogram of pure water weighed out in vacuum at its temperature of maximum density.*

In titrimetric analysis, volumes of solutions are measured in volumetric vessels, such as flasks, pipettes, and burettes. The accurate marking of these vessels with notches corresponding to definite volumes (capacities) is known as *graduation*, while checking the correctness of the volumes marked off by these notches is called *calibration of volumetric glassware*. The graduation and calibration of volumetric glassware is done by weighing pure water contained in them (volumetric flasks) or issued from them (pipettes and burettes). The weighing operation is carried out not at a temperature of $+4°C$ and not in vacuum but under atmospheric pressure and in vessels which expand with heat. Three corrections are therefore introduced into the graduation and calibration of volumetric glassware: (a) for the temperature expansion of water, (b) for the temperature expansion of the vessel, and (c) for weighing in air.

In order to avoid errors during analytical operations with volumetric glassware at various temperatures, the vessels are graduated so that the capacity of a vessel should be equal to the indicated (nominal) volume not at the temperature at which the vessel was graduated, but at the temperature normal for all laboratories, i.e. at 20°C. Hence, when grad-

uating a vessel for the same volume but at various temperatures, different quantities of water are weighed out.

When graduating and calibrating volumetric glassware by weighing, take all necessary data from Table 10 in the Appendix. The Table indicates the quantities of water that should be weighed out with brass weights in a glass vessel at various temperatures, so that the volume of the water at 20°C will be equal to precisely one true litre. One thousandth of a litre is called the *apparent or calibrating mass of water.*

Since during the graduation and calibration of volumetric glassware comparatively large masses of water are weighed out (up to 1 or 2 kg), weighing should be done on chemical balances by methods which rule out any risk of error due to the inequality of beams.

Problems

1. What quantity, in grams, of distilled water should be weighed out with brass weights at 20°C to measure out a true litre?
2. What quantity, in grams, of distilled water should be weighed out with brass weights at 15°C so that at 20°C its volume will be one litre?
3. Will a kilogram of water weighed out in normal conditions occupy a volume greater or less than a true litre?
4. To graduate two volumetric flasks, one kilogram of water was accurately weighed out. Weighing was done with brass weights for the first flask and platinum weights for the second. Which flask has the smaller correction?
5. What quantity, in grams, of water should be weighed out at 18.2°C so that its volume at 20°C will be 250 ml?
6. What quantity, in grams, of water should be weighed out to calibrate a 500-ml flask at 24.6°C?
7. Calculate the mass of the weights in the pan of a balance to substitute for a flask calibrated for 500 ml counterbalanced with 500 g weights, if the calibration is done at 22.6°C.
8. The same at 15.8°C for a 250-ml flask.
9. The same at 24.4°C for a 200-ml flask.
10. The same at 16.0°C for a 150-ml flask.
11. The same at 23.6°C for a 100-ml flask.
12. The same at 20.0°C for a 50-ml flask.

13. When a volumetric flask was calibrated, the following data were obtained: nominal capacity of the flask, 1000 ml at 20°C; the mass of water filled in the flask to the mark, 997.20 g; the temperature, 17.0°C. What is the true volume (V_{true}) and the correction (ΔV) of the flask?

14. The nominal capacity of a volumetric flask is 500 ml at 20°C; the mass of water filled into the flask to the mark, 498.80 g; the temperature, 21.6°C. Determine the true volume (V_{true}) and the correction (ΔV) of the flask.

15. The following data were obtained during the calibration of a volumetric flask: the temperature during the test (t_1), 15.2°C; the nominal volume (V_{nom}), 1000 ml; the temperature at which the flask has an accurately stated capacity (t_2), 20°C; the mass of the weights which counterbalance the empty flask (m), 1000 g; the sum of weights (Δm) which equilibrate the balance after removing the 1000 g weight and filling the flask with water to the mark, 2.87 g. What is the true volume of the flask (V_{true}) and the correction (ΔV) if $\Delta V = V_{true} - V_{nom}$?

16. As in the previous problem, determine V_{true} and ΔV of a flask, given: $V_{nom} = 500$ ml; $m = 500$ g; $\Delta m = 1.42$ g; $t_1 = 17.8$°C and $t_2 = 20$°C.

17. Do the same given the following conditions: $V_{nom} = 250$ ml; $m = 250$ g; $\Delta m = 0.72$ g; $t_1 = 18.2$°C and $t_2 = 20$°C.

18. Do the same given the following conditions: $V_{nom} = 200$ ml; $m = 200$ g; $\Delta m = 0.54$ g; $t_1 = 26.4$°C and $t_2 = 20$°C.

19. Do the same given the following conditions: $V_{nom} = 150$ ml; $m = 150$ g; $\Delta m = 0.40$ g; $t_1 = 22.6$°C and $t_2 = 20$°C.

20. Do the same given the following conditions: $V_{nom} = 100$ ml; $m = 100$ g; $\Delta m = 0.29$ g; $t_1 = 15.0$°C and $t_2 = 20$°C.

21. A pipette was calibrated by filling it with water three times to the mark at 25.4°C and weighing the water. The results were as follows: 19.962, 19.958, and 19.966 g. What are V_{true} and ΔV of the pipette?

22. A pipette was calibrated. The results were as follows: the mass of an empty weighing bottle, 24.648 g; the mass of the weighing bottle holding the water taken from the pipette,

49.574, 49.584, and 49.588 g. The temperature of the test, 19.2°C. Determine the true capacity of the pipette and the correction.

23. During the graduation of a pipette for 20 ml, two temporary marks were put on the glass. The distance between the marks is 50 mm. The ambient temperature at the moment of the test was 22.2°C. The mass of the water taken from the pipette when filled to the first (lower) mark is 19.460 g, and to the upper mark, 20.520 g. At what distance from the lower mark should the permanent mark be placed?

24. At what distance from the lower temporary mark should the permanent one be placed on a pipette if the following results were obtained during its graduation: distance between the marks, 100 mm; t of the test, 18.8°C; the mass of the water issued from the pipette when filled to the lower mark, 49.5300 g, and to the upper mark, 50.3200 g?

25. During the graduation of a pipette the following results were obtained: the distance between the marks, 50 mm; the mass of an empty weighing bottle, 38.4652 g; the mass of the bottle holding the water taken from the pipette filled to the lower temporary mark: (1) 57.9552 g; (2) 57.9562 g; and (3) 57.9542 g; the mass of the weighing bottle containing water taken from the pipette from the upper mark (into the same weighing bottle): (1) 59.0072 g, (2) 59.0052 g, and (3) 59.0032; g; the temperature at the moment of the test, 21.2°C. Determine the point where the permanent mark should be placed.

26. During the graduation of a pipette the following data were obtained: the distance between the temporary marks, 100 mm; the mass of an empty weighing bottle, 53.4200 g; the mass of the same bottle holding the water issued from the pipette filled to the lower mark: (1) 102.2028 g, (2) 102.1900 g, and (3) 102.2050 g; and to the upper mark: (1) 104.1992 g, (2) 104.2003 g, and (3) 104.1972 g; the ambient temperature at the moment of the test, 19.8°C. At what distance from the lower temporary mark should the permanent mark be placed? What volume will it measure out?

27. The following results were obtained during the graduation of a pipette: the ambient temperature at the moment of the test, 16.8°C; the distance between the temporary marks 50 mm; the mass of water issued from the pipette filled to

the upper mark, 24.7330 g; and to the lower mark, 23.9450 g. Where should the permanent mark be placed? What volume will it measure out?

28. During the graduation of a pipette two temporary marks were placed at a distance of 100 mm from each other. At 24.8°C the mass of water issued from the pipette filled to the lower mark is 97.6250 g, and to the upper mark, 99.4320 g. Where should the permanent mark be placed? What volume will it measure out?

29. The mass of a weighing bottle holding water taken from a burette from the zero mark to the 30th division is 72.210 g at 26.2°C. The mass of an empty weighing bottle is 42.344 g. What are the true volume and the correction corresponding to this point of the burette?

30. Construct a correction curve for a burette on the basis of the data in the table below:

V_{nom}, ml	Mass of water m, g	t, °C	Calibrating mass of water m_t	V_{true}	ΔV
5	4.986	24.8			
10	9.984	24.8			
15	14.972	24.8			
20	19.964	24.8			
25	24.930	24.8			
30	29.868	24.8			
35	34.845	22.8			
40	39.830	22.8			
45	44.780	22.8			
50	49.730	22.8			

C. Expressing the concentration of a standard solution

Standard solution is the solution of a substance of known concentration which reacts with another substance to be determined.

Standard substance is the substance from which a standard solution is prepared.

Titre against standard substance (T_{st}), or simply **titre**, is the number of grams of the standard substance contained in 1 ml of the standard solution.

Titre against desired substance ($T_{st/des}$) is the number of grams of the desired substance equivalent to the quantity of the standard substance contained in 1 ml of the standard solution, i.e. titrated by one millilitre of the solution.

Normality is the number of gram-equivalents of a standard substance contained in one litre (or milligram-equivalents in 1 ml) of a given standard solution.

Correction factor (K), or simply correction, is a number showing how many times the normality of a given standard solution is greater than one of the following accurate concentrations: 0.1, 0.2, 0.5, 0.01, 0.02, 0.05, . . . N.

Problems

1. A sample of pure NaCl weighing 5.9120 g is dissolved in a 1-litre volumetric flask. The solution is then diluted to the mark. What is the titre of the obtained solution against the standard substance?

2. A sample of pure KCl weighing 3.8260 g is dissolved to make 500 ml of solution. What is its titre against (a) KCl, (b) Cl?

3. A sample of pure iron weighing 2.8120 g is dissolved in hydrochloric acid, and the solution diluted to make 500 ml. Determine the titre of the solution against (a) Fe, (b) $FeCl_2$.

4. A sample of pure Na_2CO_3 weighing 1.3540 g is dissolved in a volumetric flask (250 ml) and water added to the mark. What is the titre of the solution against (a) Na_2CO_3, (b) Na_2O?

5. The label on a flask reads "KOH; T = 0.005742". How many grams of KOH is contained in (a) 10 ml, (b) 25 ml (c) 100 ml of the solution?

6. How many grams of NaOH are contained in (a) 10 ml, (b) 250 ml, (c) 1000 ml of a solution whose titre against NaOH is 0.004120?

7. How many grams of iodine are contained in 15.50 ml of a solution whose titre is 0.01263?

8. What quantity of H_2SO_4 is contained in (a) 28.60 ml, (b) 12.54 ml of a solution whose titre is 0.005146?

9. If 26.75 ml of a solution of hydrochloric acid whose titre is 0.003782 were spent for titration, what quantity, in grams, of HCl was spent to react with the desired substance?

10. If 18.54 ml of a NaOH solution whose titre is 0.003980 were spent for titration, how many grams of NaOH reacted with the desired substance?

11. The titre of a solution of NaOH is 0.04000. What is its titre against HCl?

12. The titre of HCl solution is 0.03647. What is its titre against KOH?

13. The titre of $AgNO_3$ solution is 0.01702. Determine its titre against NaCl.

14. The titre of KCl solution is 0.003756. Determine its titre against Ag.

15. A solution contains 2.8640 g of KOH in one litre. What is its titre against H_2SO_4?

16. A sample of pure NaCl weighing 0.2968 g is dissolved in a 250-ml volumetric flask. What is the titre of the solution against Ag?

17. $T_{NaOH} = 0.00400$. Find $T_{NaOH/HCl}$.

18. $T_{HCl} = 0.003647$. Find $T_{HCl/KOH}$.

19. $T_{KOH} = 0.005842$. Find T_{KOH/H_2SO_4}.

20. $T_{H_2SO_4} = 0.004674$. Find $T_{H_2SO_4/Na_2O}$.

21. $T_{NaOH} = 0.04102$. Find T_{NaOH/SO_3}.

22. $T_{HCl} = 0.03840$. Find T_{HCl/K_2O}.

23. $T_{AgNO_3} = 0.01730$. Find $T_{AgNO_3/Na}$.

24. $T_{AgNO_3} = 0.01882$. Find $T_{AgNO_3/Cl}$.

25. If 10.00 ml of a standard solution of NaOH with the titre $T_{NaOH/HCl} = 0.003874$ were spent for the titration of hydrochloric acid, how many grams of HCl are contained in the solution?

26. If 20.00 ml of a standard solution of HCl with the titre $T_{HCl/NaOH} = 0.00800$ were spent for titration of NaOH solution, how many grams of NaOH are contained in the solution?

27. If 28.35 ml of KOH solution with the titre $T_{KOH/H_2SO_4} = 0.04890$ were spent for titration of sulphuric acid, how many grams of H_2SO_4 are contained in the solution?

28. If 19.95 ml of $AgNO_3$ solution with the titre $T_{AgNO_3/Cl} = 0.03640$ were spent for titration of NaCl solution, how many grams of Cl does the solution contain?

29. If 10.00 ml of KOH solution with the titre $T_{KOH/Cl}$ = = 0.03565 were spent to titrate sulphuric acid, how many grams of H_2SO_4 does the solution contain?

30. If 20.00 ml of HCl solution with the titre $T_{HCl/KOH}$ = = 0.02820 were spent to titrate NaOH solution, how many grams of NaOH does the solution contain?

31. $T_{H_2SO_4/KOH} = 0.005820$. Find $T_{H_2SO_4}$.

32. $T_{NaOH/HCl} = 0.003952$. Find T_{NaOH}.

33. Work out a general formula for the conversion of T_{st} into $T_{st/des}$.

34. Work out a general formula for the conversion of $T_{st/des}$ into T_{st}.

35. $T_{KOH} = 0.05611$. Find the normality of KOH.

36. $T_{HCl} = 0.003647$. Find the normality of HCl.

37. $T_{NaCl} = 0.005902$. Find the normality of NaCl.

38. $T_{H_2SO_4} = 0.004990$. Find the normality of H_2SO_4.

39. $T_{NaOH} = 0.003882$. Find the normality of NaOH.

40. $T_{AgNO_3} = 0.01598$. Find the normality.

41. $T_{NaCl} = 0.005420$. Find the normality.

42. $T_{KCl/Cl} = 0.003674$. Find the normality.

43. $T_{K_2Cr_2O_7} = 0.004650$. Find the normality of the solution: (a) for an exchange reaction; (b) for a redox reaction in which potassium dichromate is converted into $CrCl_3$.

44. $T_{KMnO_4} = 0.002980$. Find the normality of the solution in reactions where potassium permanganate is converted into (a) MnO_2 and (b) $MnSO_4$.

45. $T_{KOH/HCl} = 0.003465$. Find the normality.

46. $T_{HCl/NaOH} = 0.003984$. Find the normality.

47. $T_{H_2SO_4/K_2O} = 0.004615$. Find the normality.

48. $T_{NaOH/SO_3} = 0.004152$. Find the normality.

49. Work out a formula for the conversion of T_{st} to normality (N).

50. Work out a formula for the conversion of N of a standard solution to T_{st}.

51. Work out a formula for the conversion of $T_{st/des}$ to N.

52. Work out a formula for the conversion of N to $T_{st/des}$.

53. If 19.50 ml of 0.9640N KOH are spent to titrate 20.00 ml of HCl solution, determine the normality of the HCl solution.

54. If 28.40 ml of a 0.1265N solution of sulphuric acid are spent to titrate 25.00 ml of a KOH solution, determine the normality of the KOH solution.

55. If 18.25 ml of a 0.1140*N* solution of $AgNO_3$ are spent for the titration of 20.00 ml of an NaCl solution, determine the normality of the NaCl solution.

56. If 22.60 ml of a 0.9890*N* solution of HCl are spent for the titration of 25.00 ml of an NaOH solution, determine the normality of the NaOH solution.

57. If 21.55 ml of an NaOH solution with $T_{NaOH} = 0.008110$ are spent for the titration of 20.00 ml of sulphuric acid, determine the normality of the sulphuric acid.

58. If 24.85 ml of a KOH solution with $T_{KOH} = 0.02806$ are spent to titrate 25.00 ml of an HCl solution, determine the normality of the hydrochloric acid.

59. If 23.25 ml of HCl with $T_{HCl} = 0.007352$ are spent for the titration of 25.00 ml of a KOH solution, determine the normality of the KOH solution.

60. If 19.10 ml of sulphuric acid with $T_{H_2SO_4} = 0.01000$ are spent for the titration of 20.00 ml of alkali solution, what is the normality of the alkali solution? Can we determine its titre?

61. If 30.20 ml of an $AgNO_3$ solution ($T_{AgNO_3} = 0.1245$) are spent for the titration of a KCl solution, how many grams of KCl are contained in the solution? Can we establish its normality?

62. If 25.40 ml of a 0.2140*N* solution of NaOH are spent for the titration of sulphuric acid, how many grams of H_2SO_4 does the solution contain?

63. If 23.30 ml of an NaOH solution with $T_{NaOH/H_2SO_4} = 0.04980$ are required to titrate 25.00 ml of HCl of unknown concentration, determine the normality of the HCl solution.

64. If 25.82 ml of an NaOH solution are spent to titrate 25.00 ml of an HCl solution with $T_{HCl/NaOH} = 0.01122$, determine the normality of the NaOH solution.

65. If 18.40 ml of sulphuric acid are spent for the titration of 20.00 ml of a KOH solution with $T_{KOH/HCl} = 0.07255$, determine the normality of the solution.

66. If 23.20 ml of an $AgNO_3$ solution of unknown concentration are spent for the titration of 25.00 ml of a KCl solution with $T_{KCl/Ag} = 0.01000$, what is the normality of the $AgNO_3$ solution?

67. If 25.00 ml of an HCl solution are spent for the titration of 25.00 ml of an NaOH solution with $T_{NaOH/H_2SO_4} =$

= 0.004904, what is the normality of the latter solution?

68. If 20.00 ml of a KOH solution of unknown concentration are spent for the titration of 20.00 ml of an HCl solution with $T_{HCl/NaOH}$ = 0.003954, what is the normality of the latter solution?

69. $T_{KMnO_4/Fe}$ = 0.002830. What is the normality of the solution in reactions, where the permanganate is converted into $MnSO_4$ and in reactions where it is converted into MnO_2?

70. $T_{K_2Cr_2O_7/Fe}$ = 0.01126. Determine the normality of the solution if it is to be used in reactions where the dichromate is converted into $CrCl_3$.

71. The normality of a KOH solution is 0.1124. Determine K_{KOH}.

72. The normality of an HCl solution is 0.0954. Determine K_{HCl}.

73. The normality of a KOH solution is 0.04860. Determine K_{KOH}.

74. The normality of an NaCl solution is 0.01980. Determine K_{NaCl}.

75. Determine K_{HCl} if T_{HCl} is 0.001842.

76. Determine $K_{H_2SO_4}$ if $T_{H_2SO_4}$ is 0.009860.

77. Determine K_{NaOH} if T_{NaOH} is 0.02120.

78. Determine K_{KOH} if T_{KOH} is 0.01122.

79. Determine K_{HCl} if $T_{HCl/KOH}$ is 0.005412.

80. Determine K_{NaOH} if $T_{NaOH/HCl}$ is 0.01890.

81. Determine K_{AgNO_3} if $T_{AgNO_3/Cl}$ is 0.007024.

82. Determine $K_{H_2SO_4}$ if $T_{H_2SO_4/Na_2O}$ = 0.003904.

83. K_{NaOH} is 1.1430 for 0.1N. Determine T_{NaOH}.

84. K_{HCl} = 1.0840 for 0.2N. Determine T_{HCl}.

85. K_{KOH} = 0.9246 for 0.05N. Determine T_{KOH}.

86. $K_{H_2SO_4}$ = 0.8542 for 0.01N. Determine $T_{H_2SO_4}$.

87. K_{NaOH} = 1.2040 for 0.5N. Determine $T_{NaOH/HCl}$.

88. K_{HCl} = 0.8642 for 0.02N. Determine $T_{HCl/KOH}$.

89. K_{KOH} = 1.0580 for 0.5N. What is the normality of KOH?

90. K_{KCl} = 0.9544 for 0.2N. What is the normality of KCl?

In titrimetric analysis several standard solutions of various concentrations are often mixed together, with the quantities of the different substances then being added together or

subtracted in order to find out which substance remains in excess and in what quantity. It is very difficult and of no benefit to do these calculations in the usual way, calculating the quantity of each individual substance contained in each solution. It is more convenient to simply convert all concentrations involved to one common normality equal to unity.

Example 1. If 25 ml of a $0.22N$ solution of an acid are mixed with 24 ml of a $0.25N$ solution of an alkali, what is the reaction of the resultant mixture?

Solution. Adjust the concentrations of both solutions to $1N$ using the basic rule of titrimetric analysis:

$$\frac{25}{x} = \frac{1}{0.22} \text{ and } \frac{24}{y} = \frac{1}{0.25}$$

$$x = 25 \times 0.22 = 5.5 \text{ ml of } 1N \text{ acid solution}$$

$$y = 24 \times 0.25 = 6.0 \text{ ml of } 1N \text{ alkali solution.}$$

Since the alkali is present in greater quantity (6.0—5.5 = = 0.5 ml as $1N$ solution) the solution is alkaline.

When performing such calculations one should clearly understand the meaning of the product of the solution volume and its normality. The product shows what volume of an exactly uninormal solution contains the same amount of solute that is contained in a given volume of a solution of specified normality. But one litre of a uninormal solution contains one gram-equivalent, while 1 ml contains 1 mg-equivalent of solute. Hence, the product of the volume (in ml) of a solution and its normality gives the number of milligram-equivalents of solute contained in the solution.

Example 2. If 50.00 ml of a $0.09840N$ solution of sulphuric acid are mixed with 25.15 ml of a $0.2050N$ solution of NaOH, which of the reactants remains in excess? What is the amount of this excess?

Solution. As in the previous example, we must first recalculate the volumes of both solutions as uninormal:

$$50.00 \times 0.09840 = 4.920 \text{ ml (mg-equiv) } H_2SO_4$$

$$25.15 \times 0.2050 = 5.156 \text{ ml (mg-equiv) NaOH.}$$

Hence sodium hydroxide is in excess (5.156 — 4.920 =

= 0.236 mg-equiv, or ml of 1*N* solution). In order to express the excess of sodium hydroxide in grams, multiply by the milligram-equivalent of NaOH, or, the same thing, by the NaOH content in 1 ml of a uninormal solution:

$$0.236 \times \frac{40.00}{1000} = 0.00944 \text{ g.}$$

Example 3. If 2.00 ml of a 0.100*N* solution of HCl are mixed with 20.00 ml of a 0.0800*N* solution of KOH, determine the normality of the resultant solution of KOH.

Solution. Adjust the concentrations of both solutions to 1*N*.

$$\begin{array}{r} 20.00 \times 0.0800 = 1.600 \text{ ml of } 1N \text{ KOH (mg-equiv)} \\ - \quad 2.00 \times 0.100 = 0.200 \text{ ml of } 1N \text{ HCl (mg-equiv)} \\ \hline 1.400 \text{ ml of } 1N \text{ KOH (mg-equiv)} \end{array}$$

The difference between the volumes indicates the amount of KOH excess contained in the resultant solution, equal to the amount of KOH contained in 1.4 ml of an exactly uninormal solution. But this amount of KOH is not actually contained in 1.4 ml but in the combined volume of the two solutions: 2.00 + 20.00 = 22.00 ml. Hence the resultant KOH solution will not be uninormal, viz.:

$$\frac{1 \times 1.40}{22.00} = 0.64N.$$

The same result can be obtained in a different way:

22.00 ml contain 1.400 mg-equiv of KOH
1 ml contains x mg-equiv of KOH.

The calculation shows that x = 0.064 mg-equiv in 1 ml or 0.064 gram-equivalents in one litre. In other words, the KOH concentration of the resultant solution is 0.064*N*.

91. If 50.00 ml of a 0.2000*N* solution of KOH are mixed with 25.00 ml of a 0.3000*N* solution of HCl, what is the reaction of the resultant solution?

92. If 10 ml of a 0.050*N* alkali solution are mixed with 5.0 ml of a 0.10*N* acid solution, what is the reaction of the resultant solution?

93. If 25.00 ml of a 0.0987*N* solution of HCl are mixed with 24.50 ml of a 0.1020*N* solution of NaOH, what substance is in excess?

94. If 50.00 ml of a 0.0520*N* HCl are treated with 40.00 ml of KOH solution ($K = 1.354$ for 0.05*N*), what substance is left in excess in the resultant solution?

95. The following solutions were poured into a flask one after another: 10.00 ml of 0.1120*N* HCl, 5.20 ml of 0.2000*N* KOH, 2.30 ml of 0.0500*N* H_2SO_4, and 5.10 ml of NaOH solution in which $K = 1.080$ for 0.05*N*. How does the resultant solution react?

96. To neutralize 25.00 ml of a 0.1050*N* solution of KOH 15.00 ml of HCl ($K = 1.100$ for 0.1*N*) and 20.00 ml of H_2SO_4 ($K = 0.9950$ for 0.05*N*) were added to it. What is the reaction of the resultant solution?

97. If 50.00 ml of a 0.1150*N* solution of HCl are mixed with 25.00 ml of a 0.0952*N* solution of KOH, what quantity, in grams, of hydrogen chloride remains in excess?

98. If 100.0 ml of potassium hydroxide solution ($K = 1.095$ for 0.1*N*) are mixed with 100.0 ml of hydrochloric acid ($K = 0.9920$ for 0.05*N*), which of the reactants and in what quantity remains unreacted?

99. Determine the normality of a KOH solution obtained by mixing 2.00 ml of 0.8970*N* HCl and 25.0 ml of KOH solution ($K = 1.085$ for 0.1*N*).

100. Determine the concentration of sulphuric acid in a solution obtained by mixing 20.00 ml of H_2SO_4 ($K = 0.9140$ for 0.2*N*) with 4.00 ml of NaOH ($K = 1.1800$ for 0.05*N*).

101. If 25.00 ml of sulphuric acid ($K = 1.002$ for 0.05*N*) and 5.23 ml of KOH solution ($K = 0.9350$ for 0.03*N*) are mixed together, determine the titre of the acid in the resultant solution.

102. If 25.00 ml of KOH solution ($K = 1.200$ for 0.1*N*) are mixed with 2.50 ml of 1.00*N* HCl, which of the reactants is in excess? What is its titre in the resultant solution?

CHAPTER FOUR

OXIDATION-REDUCTION METHODS (OXIDIMETRY)

A. Fundamental Theory of Oxidation-Reduction Methods

Oxidation-reduction methods (*oxidimetry*) *are titrimetric* (*volumetric*) *methods of analysis based on the oxidation-reduction reaction.* In redox reactions the atoms or ions of one substance, the reducer, give off or donate their electrons to the atoms or ions of another substance, oxidant. The degree of oxidation of some of the elements involved in redox reactions is therefore changed. The oxidant atoms gain electrons, which decreases their degree of oxidation; in other words they are reduced. The atoms of reducing substances give off their electrons to oxidants and thus increase their degree of oxidation. They are said to be oxidized.

To set up the equation of a redox reaction it is necessary to select coefficients so that the number of electrons given off by a reducing substance is equal to the number of electrons accepted by the oxidant. To attain this, it is necessary to know the following: (1) chemical formulas of the oxidant and reducer; (2) chemical formulas of the products of the oxidation and reduction processes.

Example 1. Write the equation of the redox reaction between $FeSO_4$ and $KMnO_4$, when $FeSO_4$ converts into $Fe_2(SO_4)_3$ and $KMnO_4$ into $MnSO_4$.

Solution.

1. Write down the formulas of the oxidant and the reducer, put a plus sign between them, and, leaving a gap, write the formulas of the products of oxidation and reduction:

$$FeSO_4 + KMnO_4 + \ldots \longrightarrow Fe_2(SO_4)_3 + MnSO_4 + \ldots .$$

2. Find the chemical elements which change their degree of oxidation in this reaction and write them above the chem-

ical symbols:

$$\overset{+2}{FeSO_4} + \overset{+7}{KMnO_4} + \ldots \rightarrow \overset{+3}{Fe_2(SO_4)_3} + \overset{+2}{MnSO_4} + \ldots .$$

3. Write underneath the number of electrons given off or accepted by the elements in the reaction. Find these numbers by subtracting a smaller degree of oxidation of a given element from a greater one. For manganese: $(+7)-(+2) = 5$; for iron: $(+3)-(+2) = 1$:

$$\begin{array}{l} \overset{+2}{FeSO_4} + \overset{+7}{KMnO_4} + \ldots \rightarrow \overset{+3}{Fe_2(SO_4)_3} + \overset{+2}{MnSO_4} + \ldots . \\ \begin{array}{ll} 1 & 5 \\ 2 & 10 \end{array} \end{array}$$

The number of Fe atoms on the right-hand side of the equation must be even (Fe_2), and so the ratio 1 : 5 should be changed to 2 : 10.

4. Substitute the found numbers of electrons donated and accepted by the oxidant and reducer into their formulas as coefficients (crosswise):

$$10FeSO_4 + 2KMnO_4 + \ldots \rightarrow Fa_2(SO_4)_3 + MnSO_4 + \ldots .$$

5. The coefficients for the oxidant and reducer should be placed before the corresponding reaction products on the right-hand side:

$$10FeSO_4 + 2KMnO_4 + \ldots \rightarrow 5Fe_2(SO_4)_3 + 2MnSO_4 + \ldots .$$

6. The right-hand side of the equation, unlike the left-hand side, has no potassium ions. Therefore, we add K_2SO_4. Now the right-hand side of the equation has 18 SO_4^{2-} ions, while on the left-hand side there are only 10. Add eight molecules of H_2SO_4 to the left-hand side:

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \rightarrow 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4$$

7. Finally, count the number of hydrogen and oxygen atoms on both sides of the equation. The left-hand side has 16 hydrogens and 8 oxygens in excess. Therefore add 8 molecules of water to the right-hand side of the equation. Check the number of the other atoms and put the sign of equality between the two sides of the equation:

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O.$$

In order to find out in what direction the given oxidation-reduction reaction will proceed, use Table 8 in the Appendix to compare the normal potentials (E^0) of the systems taking part in the reaction. The system having a greater potential is the oxidant and that having a smaller potential is the reducer.

Example 2. In what direction will the reaction described above proceed?

Solution. Two systems are involved in the reaction, namely: Mn^{7+}/Mn^{2+} and Fe^{2+}/Fe^{3+}. Consult Table 8 to find the following:

$$E^0_{Mn^{7+}/Mn^{2+}} = +1.52 \text{ V and } E^0_{Fe^{2+}/Fe^{3+}} = +0.77 \text{ V}.$$

Hence the permanganate is the oxidant in the reaction and it will oxidize Fe^{2+} to Fe^{3+}. But Fe^{3+} cannot oxidize $MnSO_4$ to $KMnO_4$, i.e. in effect the given reaction occurs only from left to right.

Electromotive Force of a Reaction. The difference between the normal potentials of systems taking part in a reaction is called the *electromotive force of the reaction.* The higher the electromotive force (e.m.f.), the more energetic the reaction. Therefore, in order to decide which of the reducing agents that are present simultaneously in the solution is to be oxidized the first, it is necessary to find the e.m.f. of both possible reactions. The reaction with the greater e.m.f. will occur first.

Example 3. A solution contains Cl^- and SO_3^{2-} ions. Which of them will be oxidized first by permanganate if their concentrations are approximately the same?

Solution. Consult the Table to find that

$$E^0_{SO_3^{2-}/SO_4^{2-}} = +0.20 \text{ V}; \quad E^0_{Cl^-/Cl^0} = +1.36 \text{ V};$$

$$E^0_{MnO_4^-/Mn^{2+}} = +1.52 \text{ V}.$$

The e.m.f. of oxidation of the SO_3^{2-} ions with the permanganate is $1.52 - 0.20 = 1.32$ V, and of the Cl^- ions, $1.52 - 1.36 = 0.16$ V. Hence the SO_3^{2-} ion will be oxidized the first.

These calculations also show that the chloride ion will not interfere with the quantitative determination of the SO_3^{2-} ions because of the great difference in their e.m.f. in the reaction of oxidation with potassium permanganate.

Problems

Write equations for the following oxidation-reduction reactions:

1. $Zn + HCl \rightarrow ZnCL_2 + H_2$
2. $Al + H_2SO_4 \rightarrow Al_2(SO_4)_3 + H_2$
3. $Zn + KOH \rightarrow K_2ZnO_2 + H_2$
4. $Al + KOH \rightarrow K_3AlO_3 + H_2$
5. $C + O_2 \rightarrow CO_2$
6. $Fe + S \rightarrow FeS$
7. $Al + S \rightarrow Al_2S_3$
8. $C + HNO_3 \rightarrow CO_2 + NO + \ldots$
9. $Cu + H_2SO_4 \rightarrow CuSO_4 + SO_2 + \ldots$
10. $Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO + \ldots$
11. $Hg + HNO_3 \rightarrow Hg(NO_3)_2 + NO + \ldots$
12. $Zn + HNO_3 \rightarrow Zn(NO_3)_2 + NH_4NO_3 + \ldots$
13. $Sn + HNO_3 + \ldots \rightarrow H_2SnO_3 + NO$
14. $S + HNO_3 \rightarrow H_2SO_4 + NO$
15. $P + HNO_3 + \ldots \rightarrow H_3PO_4 + NO$
16. $H_2S + O_2 \rightarrow H_2O + SO_2$
17. $H_2S + HNO_3 \rightarrow H_2SO_4 + NO + \ldots$
18. $H_2S + HNO_3 \rightarrow S + NO + \ldots$
19. $CrCl_3 + Br_2 + \ldots \rightarrow K_2CrO_4 + KBr + \ldots$
20. $Cr_2(SO_4)_3 + Br_2 + \ldots \rightarrow Na_2CrO_4 + NaBr + \ldots$
21. $FeCl_2 + Br_2 + \ldots \rightarrow Fe(OH)_3 + KBr + \ldots$
22. $Fe + HNO_3 + \ldots \rightarrow FeCl_3 + NO + \ldots$
23. $Fe_2O_3 + C \rightarrow Fe + CO$
24. $CuO + C \rightarrow Cu + CO$
25. $NaCl + MnO_2 + \ldots \rightarrow Cl_2 + MnSO_4 + \ldots$
26. $KBr + MnO_2 + \ldots \rightarrow Br_2 + MnSO_4 + \ldots$
27. $NaBr + H_2SO_4 \rightarrow Br_2 + SO_2 + \ldots$
28. $KI + H_2SO_4 \rightarrow I_2 + SO_2 + \ldots$
29. $HgCl_2 + SnCl_2 \rightarrow Hg_2Cl_2 + SnCl_4$
30. $HgCl_2 + SnCl_2 \rightarrow Hg + SnCl_4$
31. $BaSO_4 + C \rightarrow BaS + CO$
32. $FeCl_3 + H_2S \rightarrow FeCl_2 + S + \ldots$

33. $K_2Cr_2O_7 + H_2S + \ldots \rightarrow Cr_2(SO_4)_3 + S + \ldots$
34. $KI + K_2Cr_2O_7 + \ldots \rightarrow I_2 + Cr_2(SO_4)_3 + \ldots$
35. $KBr + K_2Cr_2O_7 + \ldots \rightarrow Br_2 + Cr_2(SO_4)_3 + \ldots$
36. $HBr + K_2Cr_2O_7 + \ldots \rightarrow Br_2 + CrCl_3 + \ldots$
37. $HBr + K_2Cr_2O_7 + \ldots \rightarrow Br_2 + Cr_2(SO_4)_3 + \ldots$
38. $SO_2 + K_2Cr_2O_7 + \ldots \rightarrow Cr_2(SO_4)_3 + \ldots$
39. $FeCl_3 + SnCl_2 \rightarrow FeCl_2 + SnCl_4$
40. $FeO + CO \rightarrow Fe + CO_2$
41. $SnSO_4 + I_2 + \ldots \rightarrow Sn(SO_4)_2 + HI$
42. $H_2S + SO_2 \rightarrow S + H_2O$
43. $I_2 + \ldots \rightarrow KIO_3 + KI + \ldots$
44. $Br_2 + \ldots \rightarrow NaBrO_3 + NaBr + \ldots$
45. $Hg_2S \rightarrow HgS + Hg$
46. $NH_2Hg_2Cl \rightarrow NH_2HgCl + Hg$
47. $K_2MnO_4 + \ldots \rightarrow KMnO_4 + MnO_2 + \ldots$
48. $MnO_2 + KNO_3 + \ldots \rightarrow K_2MnO_4 + KNO_2 + \ldots$
49. $NaCl + KMnO_4 + \ldots \rightarrow Cl_2 + MnSO_4 + \ldots$
50. $HCl + KMnO_4 + \ldots \rightarrow Cl_2 + MnSO_4 + \ldots$
51. $KBr + KMnO_4 + \ldots \rightarrow Br_2 + MnSO_4 + \ldots$
52. $KMnO_4 + K_2SO_3 + \ldots \rightarrow MnSO_4 + K_2SO_4 + \ldots$
53. $KMnO_4 + K_2SO_3 + \ldots \rightarrow MnO_2 + K_2SO_4 + \ldots$
54. $MnSO_4 + KMnO_4 + \ldots \rightarrow MnO_2 + \ldots$
55. $Mn(OH)_2 + PbO_2 + \ldots \rightarrow HMnO_4 + Pb(NO_3)_2 +$
56. $Mn(OH)_3 + PbO_2 + \ldots \rightarrow HMnO_4 + Pb(NO_3)_2 + \ldots$
57. $PbCl_4 + \ldots \rightarrow PbCl_2 + HCl$
58. $Bi(OH)_3 + K_2SnO_2 \rightarrow Bi + K_2SnO_3 + \ldots$
59. $BiCl_3 + K_2SnO_2 + \ldots \rightarrow Bi + K_2SnO_3 + \ldots$
60. $As_2S_3 + HNO_3 + \ldots \rightarrow H_3AsO_4 + H_2SO_4 + NO$
61. $As_2S_5 + HNO_3 + \ldots \rightarrow H_3AsO_4 + H_2SO_4 + NO$
62. $Na_3AsO_3 + KMnO_4 + \ldots \rightarrow Na_3AsO_4 + Mn(NO_3)_2$
63. $H_3AsO_4 + KI + \ldots \rightarrow H_3AsO_3 + I_2 + KOH$

Note: In Problems 64 to 73 the oxidation with peroxides can be regarded as oxidation with free oxygen obtained by the decomposition of the peroxides, for example: $H_2O_2 = H_2O + O$.

64. $Fe(OH)_2 + H_2O_2 \rightarrow Fe(OH)_3$
65. $FeCl_2 + H_2O_2 + \ldots \rightarrow Fe(OH)_3 + \ldots$
66. $MnCl_2 + Na_2O_2 + \ldots \rightarrow H_2MnO_3 + \ldots$
67. $Mn(OH)_3 + Na_2O_2 \rightarrow H_2MnO_3 + \ldots$
68. $CrCl_3 + H_2O_2 + \ldots \rightarrow K_2CrO_4 + \ldots$

69. $CrCl_3 + Na_2O_2 + \ldots \rightarrow Na_2CrO_4 + \ldots$
70. $Cr_2(SO_4)_3 + H_2O_2 + \ldots \rightarrow K_2CrO_4 + \ldots$
71. $CuS + H_2O_2 + \ldots \rightarrow CuCl_2 + S + \ldots$
72. $NiS + H_2O_2 + \ldots \rightarrow NiCl_2 + S + \ldots$
73. $K_2Cr_2O_7 + H_2O_2 + \ldots \rightarrow CrO_5 + \ldots$

Note: In Problems 74 to 80, in writing the equations of redox reactions where the oxidants are substances with covalent bonds in their molecules (e.g. $(NH_4)_2S_2O_8$ and other persulphates), the number of electrons accepted by these substances can, as in the case with oxidation by peroxides, be determined by assuming their intermediate decomposition. For example, it can be assumed that persulphates are first decomposed to liberate free oxygen (i.e. having zero valency), which oxidizes the reducer by taking two electrons for each of its own atoms:

$$(NH_4)_2S_2O_8 + H_2O = (NH_4)_2SO_4 + H_2SO_4 + O \qquad S_2O_8^{2-} + 2e^- = 2SO_4^{2-}.$$

In other words, a molecule of persulphate acting as an oxidant requires two extra electrons. Hence when making out the relevant equations for redox reactions a 2 should be placed under the persulphate formula. For example:

$$\overset{+2}{\underset{5}{Mn}}SO_4 + (NH_4)_2\overset{0}{\underset{2}{S_2}}O_8 + \ldots \longrightarrow H\overset{+7}{Mn}O_4 + (NH_4)_2\overset{-2}{S}O_4 + \ldots .$$

Whence:

$$2MnSO_4 + 5(NH_4)_2S_2O_8 + \ldots \longrightarrow 2HMnO_4 + 5(NH_4)_2SO_4 + \ldots$$

$$2MnSO_4 + 5(NH_4)_2S_2O_8 + 8H_2O \longrightarrow 2HMnO_4 + 5(NH_4)_2SO_4 + 7H_2SO_4.$$

It can be assumed that in the formula of pyrite, FeS_2 (or $FeS \cdot S$), one sulphur atom has a degree of oxidation of -2 and the other 0. Work out the equation for the reaction of pyrite roasting:

$$\begin{array}{cccccc} +2 & -2\ 0 & 0 & +3 & -2 & +4 \\ Fe & S \cdot S & + O \rightarrow & Fe_2O_3 & + & SO_2 \\ 1 & 6\ 4 & & & & \end{array}$$

$$\underbrace{\qquad\qquad}_{11} \qquad\qquad 2$$

$\overset{+2}{Fe}$ becomes $\overset{+3}{Fe}$ by losing $1e^-$

$\overset{-2}{S}$ becomes $\overset{+4}{S}$ by losing $6e^-$

$\overset{0}{S}$ becomes $\overset{+4}{S}$ by losing $4e^-$

The whole molecule of FeS_2 loses $11e^-$

$\overset{0}{O}$ becomes $\overset{-2}{O}$ by accepting $2e^-$.

Hence the entire equation for the above reaction has the following form:

$$2FeS_2 + 11O = Fe_2O_3 + 4SO_2$$

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2.$$

All bonds in carbides and phosphides of metals (e.g. in Cr_3C_2 or Fe_3P) are covalent, and when making out the electron balance, we can, by convention, assume the degree of oxidation of all atoms to be zero. Once we admit this, it is easy to find coefficients even for such seemingly complicated equations as the equation for the reaction of iron phosphide dissolution in nitric acid (see Problem 77 below).

Coefficients for the equations of redox reactions can also be selected by the electron-ionic method. This method does not require a knowledge of the degrees of oxidation of the elements forming the molecules of the oxidant and reducer. It is necessary simply to obtain an overall balance of the number of electrons given off and accepted by all ions. This enables us to avoid working as if the molecules are first decomposed to liberate free oxygen or that they contain free atoms having zero oxidation degrees, neither of which is in fact true.

If we use this method, the equation above for the oxidation of Mn^{2+} with persulphate would be written like this:

$$Mn^{2+} + S_2O_8^{2-} \longrightarrow MnO_4^- + SO_4^{2-} \text{ (ionic equation)} \quad (1)$$

$$Mn^{2+} + 4H_2O - 5e^- = MnO_4^- + 8H^+ \text{ (oxidation of } Mn^{2+}) \quad (2)$$

$$(+2) - (-5) = +7; \quad (-1) + (+8) = +7.$$

We now add $4H_2O$, because the ion MnO_4^- has four oxygen atoms, and subtract $5e^-$ in order to balance the sum of charges on both sides of the equation. (The sum of the charges

should first be calculated for the right-hand side of the ionic equation.)

Now, in the same order, write down the process of reduction of the ion $S_2O_8^{2-}$.:

$$S_2O_8^{2-} + 2e^- = 2SO_4^{2-} \quad (3)$$

$$(-2) + (-2) = -4; \quad 2 \times (-2) = -4.$$

Equalize the quantities of electrons given off ($5e^-$) and accepted ($2e^-$) by multiplying all terms of equation (2) by 2 and of equation (3) by 5 with subsequent summation of the results:

$$\begin{array}{r} 2Mn^{2+} + 8H_2O - 10e^- = 2MnO_4^- + 16H^+ \\ 5S_2O_8^{2-} + 10e^- = 10SO_4^{2-} \\ \hline 2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O = 2MnO_4^- + 10SO_4^{2-} + 16H^+ \end{array} \quad (4)$$

Rewrite the ionic equation of the reaction (4) in molecular form, adding the ions which were not involved in the oxidation-reduction process:

$$2MnSO_4 + 5(NH_4)_2S_2O_8 + 8H_2O = 2HMnO_4 + 5(NH_4)_2SO_4 + 7H_2SO_4.$$

74. $Cr_2(SO_4)_3 + Na_2S_2O_8 + \ldots \rightarrow H_2CrO_4 + H_2SO_4 + Na_2SO_4$

75. $Mn(NO_3)_2 + Na_2S_2O_8 + H_2O \rightarrow HMnO_4 + Na_2SO_4 + H_2SO_4 + \ldots$

76. $FeS_2 + O_2 \rightarrow Fe_2O_3 + SO_2$

77. $Fe_3P + HNO_3 \rightarrow Fe(NO_3)_3 + H_3PO_4 + NO + \ldots$

78. $Fe_3P + HNO_3 \rightarrow Fe(NO_3)_3 + H_3PO_3 + NO + \ldots$

79. $Fe_3P + HCl \rightarrow FeCl_2 + PH_3 + H_2$

80. $Cr_3C_2 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + C + H_2$

81. Referring to the normal potentials of oxidation-reduction systems, decide what happens when a solution of iodine and potassium iodide is added to a solution containing a mixture of ferric and ferrous salts. Will iodine oxidize ferrous iron to ferric iron? Will ferric iron oxidize the ion I^- to free iodine?

82. In what direction will the following reaction occur

$$SnCl_4 + FeCl_2 \rightleftarrows SnCl_2 + FeCl_3.$$

83. Can the ion Cr^{3+} be oxidized to CrO_4^{2-} by bromine water in an alkaline medium?

84. Can the ion Cr^{3+} be oxidized with bromine water in an acid medium?

85. Can divalent tin be oxidized to tetravalent tin with potassium chromate in an alkaline medium?

86. Can bromine water liberate free chlorine from a NaCl solution?

87. Can the ion Cl^- be oxidized to free chlorine with sulphuric acid?

88. Will concentrated sulphuric acid oxidize ferrous iron to ferric iron?

89. Will potassium permanganate oxidize ferrous iron in an acid medium?

90. Will potassium permanganate oxidize ferrous iron in an alkaline medium, reducing itself to manganate?

91. What is the e.m.f. of the oxidation of hydrogen sulphide with hydrogen peroxide?

92. Find the e.m.f. of the reaction between potassium permanganate and sodium chloride.

93. What is the e.m.f. of the reaction between sodium iodate and hydrogen sulphide?

94. Determine the e.m.f. of the reaction of the reduction of ferric chloride with stannous chloride.

95. A solution of potassium permanganate is added gradually to an acid solution containing the ions Cl^-, Br^-, and I^-. Determine the e.m.f. of the reactions and work out what occurs in the solution.

96. A solution contains sodium sulphite and sodium oxalate. Determine the e.m.f. of the reactions and decide in what sequence these ions will be oxidized if chlorine water is gradually added.

97. Can oxalates be determined permanganatometrically if hydrochloric acid is used to build up an acid medium?

98. Can divalent tin be determined quantitatively by the iodometric method if the S^{2-} ion is present in the solution?

99. A solution contains ammonium oxalate and $FeCl_2$. Which of them will be oxidized first by chlorine water?

100. What oxidant will better oxidize phosphorous acid to phosphoric acid, hydrogen peroxide or chlorine water?

B. Permanganatometry

Direct Titration. The problems in this section are solved by following the general rules of titrimetric analysis. These are discussed in detail in textbooks on quantitative analysis

and do not therefore require special explanation. Problems requiring the preliminary calculations of samples, reagent solutions, etc. should be solved only approximately, to an accuracy of one or two significant figures. All other calculations should be as accurate as possible.

Problems

Calculation of the Masses of Samples

1. What is the gram-equivalent of $KMnO_4$ (a) in an acid medium; (b) in a neutral medium; (c) in an alkaline medium?
2. By what quantity should the molecular masses of the substances given below be divided if we want to calculate their equivalent weights in reactions with $KMnO_4$ in an acid medium: (a) $FeSO_4 \cdot 7H_2O$; (b) $Na_2C_2O_4$; (c) NaI?
3. Calculate the equivalent weights of the following ions and substances in reactions with $KMnO_4$ in an acid medium: (a) Fe^{2+}; (b) $H_2C_2O_4 \cdot 2H_2O$; (c) KI.
4. Calculate the equivalent weights of the following substances in reactions of oxidation with $KMnO_4$ in an acid medium: (a) $FeSO_4 \cdot 7H_2O$; (b) Na_2SO_3; (c) $NaNO_2$.
5. What quantity, in grams, of $KMnO_4$ is required to prepare 750 ml of an approximately 0.05*N* solution?
6. What quantity, in grams, of $KMnO_4$ should be taken to prepare 1.5 litres of an approximately 0.2*N* solution?
7. What quantity, in grams, of $KMnO_4$ is required to prepare 1250 ml of a solution whose titre against potassium permanganate is 0.001617?
8. What quantity, in grams, of $KMnO_4$ is required to prepare one litre of a solution whose $K = 1.125$ for 0.05*N*?
9. What quantity, in grams, of $KMnO_4$ should be taken to prepare 5 litres of a solution whose $T_{KMnO_4/Fe}$ is 0.005585?
10. What quantity, in grams, of $KMnO_4$ is required to prepare 800 ml of a solution whose $T_{KMnO_4/Na_2C_2O_4}$ is 0.003350?
11. What quantity, in grams, of pure $H_2C_2O_4 \cdot 2H_2O$ is required to prepare 500 ml of an approximately 0.2*N* solution?
12. What quantity, in grams, of pure $Na_2C_2O_4$ is required to prepare 200 ml of the solution needed to standardize a $KMnO_4$ solution of about 0.1*N*?

13. Calculate the mass of pure $(NH_4)_2C_2O_4 \cdot H_2O$ required to prepare 200 ml of a solution intended for the standardization of an approximately 0.05*N* solution of $KMnO_4$.

14. Calculate the mass of sodium oxalate required to prepare 250 ml of a solution intended to standardize an approximately 0.01*N* solution of $KMnO_4$.

15. To standardize a solution of $KMnO_4$ a piece of iron wire is dissolved in sulphuric acid in the absence of air. Determine the mass of wire if the capacity of a volumetric flask in which the solution will be diluted is 200 ml and the concentration of the $KMnO_4$ solution is about 0.1*N*.

16. Find the mass of an iron wire for the standardization of a $KMnO_4$ solution, if K_{KMnO_4} is 1.2 for a 0.05*N* solution and the capacity of the flask is 150 ml.

17. What quantity, in grams, of anhydrous $H_2C_2O_4$ (pure) should be taken to standardize an approximately 0.1*N* solution of $KMnO_4$ by the increment method, if about 25 ml of the solution is to be used for titration of the obtained solution of $H_2C_2O_4$?

18. What quantity, in grams, of pure $Na_2C_2O_4$ should be taken to standardize an approximately 0.05*N* $KMnO_4$ solution by the increment method?

19. What quantity, in grams, of pure $(NH_4)_2C_2O_4 \cdot H_2O$ is required to prepare a solution, if 25 ml of an approximately 0.1*N* $KMnO_4$ solution are required for its titration?

20. Iron wire is dissolved in an acid. About 30 ml of an approximately 0.1*N* $KMnO_4$ solution are used for the titration of the solution. What is the weight of the wire?

21. If 0.32 g of $H_2C_2O_4 \cdot 2H_2O$ is taken to standardize an approximately 0.1*N* $KMnO_4$ solution by the increment method, can the sample be used (the capacity of the titration burette is 50 ml)?

22. A sample of $(NH_4)_2C_2O_4 \cdot H_2O$ weighing 0.34 g is dissolved in an arbitrary amount of water, acidified, and titrated with a 0.2*N* $KMnO_4$ solution from a 25-ml burette. Is the capacity of the burette sufficient for the titration?

Standardizing the Working Solution

There are various accurate methods of titrimetric analysis, but it is important to know how to choose the simplest and most suitable one for each particular case. This skill can

only be acquired by solving analytical problems using the various methods and comparing the results with the time spent on each problem. Such comparison shows that if a problem is solved by various techniques and if in each case a final formula is used for calculation rather than intermediate calculations, then, after all cancellations, irrespective of the calculating procedure, the result will be the same.

In order to simplify titrimetric calculations, it is useful to use one general rule, namely: *if an analysis is carried out with a measuring pipette or a volumetric flask, the concentration of the standard solution is better expressed by normality N or correction K, and calculations should be based on the main proportion:*

$$V_1 : V_2 = N_2 : N_1 \quad \text{or} \quad V_2N_2 = V_1N_1.$$

If the analysis is performed by the increment method (the method of separate samples), without a volumetric flask or pipette, the concentration of the standard solution is more conveniently expressed by the titre against the substance in question. Then the amount of solute m contained in the solution is the titre of the standard solution by the desired substance multiplied by the volume of the solution used in titration: $m = T_{st/des}V$. *In the method of separate samples, the concentration of the standard solution can be expressed in terms of the standard substance, and then the proportion is used.*

$$\frac{E_{st} - E_{des}}{VT_{st} - m}$$

where E_{st} is the equivalent weight of the standard substance; E_{des} is the equivalent weight of the desired substance to be determined; T_{st} is the titre of the standard solution against the standard substance; $T_{st/des}$ is the titre of the standard solution against the desired substance; V is the volume of the standard solution spent for titration; and m is the amount of the desired substance contained in the solution.

In order to express the found amount of the desired substance in per cent, the result is multiplied by 100 and divided by the mass of the sample.

23. A sample of pure ammonium oxalate weighing 3.5740 g is dissolved in a 500-ml measuring flask. The solution

is diluted up to the mark. Determine the concentration of the solution in the following terms: (a) $T_{(NH_4)_2C_2O_4 \cdot H_2O}$; (b) $T_{(NH_4)_2C_2O_4 \cdot H_2O/KMnO_4}$; (c) N; (d) correction (K).

24. A sample of pure $H_2C_2O_4 \cdot 2H_2O$ weighing 0.7586 g is dissolved in a 250-ml volumetric flask. Determine the concentration of the solution, expressing it in (a) $T_{H_2C_2O_4 \cdot 2H_2O}$; (b) $T_{H_2C_2O_4 \cdot 2H_2O/KMnO_4}$; (c) N; (d) correction (K).

25. A sample of pure ammonium oxalate crystal hydrate weighing 0.8842 g is dissolved in water in a 250-ml volumetric flask. Calculate the concentration of the solution, expressing it as follows: (a) $T_{(NH_4)_2C_2O_4 \cdot H_2O}$; (b) $T_{(NH_4)_2C_2O_4 \cdot H_2O/KMnO_4}$; (c) N; (d) correction (K).

26. A sample of pure $Na_2C_2O_4$ weighing 0.6784 g is dissolved in a 200-ml volumetric flask. Determine the concentration of the solution, expressing it in the following: (a) (a) $T_{Na_2C_2O_4}$; (b) $T_{Na_2C_2O_4/KMnO_4}$; (c) N; (d) correction (K).

27. To standardize a solution of $KMnO_4$, another solution was prepared by dissolving 1.5020 g of $H_2C_2O_4 \cdot 2H_2O$ in water in a 250-ml volumetric flask. About 23.68 ml of the $KMnO_4$ solution are spent to titrate 25.00 ml of the second solution. Determine: (a) T_{KMnO_4}; (b) $T_{KMnO_4/H_2C_2O_4}$; (c) N; (d) correction (K_{KMnO_4}).

28. A sample of pure sodium oxalate weighing 1.2500 g is dissolved in water in a 250-ml measuring flask. If 21.20 ml of potassium permanganate solution are spent to titrate 25.00 ml of the obtained solution, determine: (a) N_{KMnO_4}; (b) K_{KMnO_4}; (c) T_{KMnO_4}.

29. A sample of pure ammonium oxalate weighing 3.500 g is dissolved in water in a 500-ml volumetric flask in order to prepare a solution for standardization of the solution of $KMnO_4$. If 24.90 ml of the $KMnO_4$ solution are spent to titrate 25.00 ml of the initial solution, determine the following: (a) N_{KMnO_4}; (b) K_{KMnO_4}; (c) T_{KMnO_4}; (d) $T_{KMnO_4/Fe}$.

30. A sample of pure $H_2C_2O_4 \cdot 2H_2O$ weighing 1.2540 g is dissolved in water in a 250-ml volumetric flask. If 22.40 ml of $KMnO_4$ are spent for the titration of 20.00 ml of this solution, determine the following: (a) N_{KMnO_4}; (b) K_{KMnO_4}; (c) $T_{KMnO_4/FeSO_4}$.

31. A sample of pure crystalline ammonium oxalate weighing 0.7120 g is dissolved in water in a 200-ml volumetric flask. If 18.90 ml of $KMnO_4$ solution are used to titrate

25.00 ml of this solution, determine the following: (a) T_{KMnO_4}; (b) $T_{KMnO_4/Fe}$.

32. A sample of anhydrous $H_2C_2O_4$ weighing 0.8530 g is dissolved in a 200-ml measuring flask in order to prepare a solution for the standardization of a $KMnO_4$ solution. If 21.20 ml of the $KMnO_4$ solution are used to titrate 20.00 ml of this solution, determine the following: (a) N_{KMnO_4}; (b) K_{KMnO_4}; (c) T_{KMnO_4}.

33. A sample of anhydrous $H_2C_2O_4$ weighing 0.06895 g is dissolved in an arbitrary amount of water and titrated with 30.82 ml of $KMnO_4$ solution. Determine the following: a) T_{KMnO_4}; (b) N_{KMnO_4}; (c) K_{KMnO_4}.

34. If 24.68 ml of a $KMnO_4$ solution are spent in the titration of a solution of 0.1522 g of $H_2C_2O_4 \cdot 2H_2O$ in an arbitrary amount of water, determine the following: (a) T_{KMnO_4}; (b) N_{KMnO_4}; (c) K_{KMnO_4}.

35. In order to standardize a $KMnO_4$ solution, 0.1152 g of electrolytic iron is dissolved in sulphuric acid, reduced, and titrated with the $KMnO_4$ solution, of which 40.35 ml are used in the process. Determine the following: (a) T_{KMnO_4}; (b) N_{KMnO_4}; (c) K_{KMnO_4}.

36. In order to standardize a solution of $KMnO_4$, 20.00 ml of $(NH_4)_2C_2O_4 \cdot H_2O$ with the titre 0.07112 are taken. The solution is diluted in a 250-ml volumetric flask with water to the mark. If 19.85 ml of the $KMnO_4$ solution are spent to titrate 25.00 ml of the prepared solution, determine K_{KMnO_4}.

37. The following data are obtained during the standardization of a $KMnO_4$ solution by the method of separate samples against pure $(NH_4)_2C_2O_4 \cdot H_2O$:

Sample	Sample mass, m, in g	Volume, V, in ml	$\frac{m}{V}$	$\frac{m}{V}$, % (of least quantity)	$T_{KMnO_4} = \frac{m}{V} F$
1	0.1910	26.80			
2	0.1743	23.40			
3	0.1593	21.85			
4	0.1834	25.20			
5	0.2104	28.80			

Determine the mean value of T_{KMnO_4}, disregarding widely differing results.

38. The following results were obtained during the standardization of a $KMnO_4$ solution by the method of separate samples against $H_2C_2O_4 \cdot 2H_2O$:

Sample	Sample mass, m, in g	Volume, V, in ml	$\frac{m}{V}$	$\frac{m}{V}$, % (of least quantity)	$T_{KMnO_4} = \frac{m}{V} F$
1	0.1076	33.90			
2	0.1001	31.26			
3	0.0836	27.15			
4	0.0760	24.95			
5	0.0682	22.06			

Determine the mean value of T_{KMnO_4}, disregarding widely differing results.

39. Calculate the titrimetric factor for the calculation of the results of standardization of a $KMnO_4$ solution against $(NH_4)_2C_2O_4 \cdot H_2O$.

40. Calculate the titrimetric factor for the calculation of the result of standardization of a $KMnO_4$ solution against $Na_2C_2O_4$.

41. A sample of $Na_2C_2O_4$ weighing 1.2640 g is dissolved in water in a 200-ml volumetric flask. What quantity, in ml, of a $KMnO_4$ solution ($K = 0.9864$ for $0.1N$) will be spent for the titration of 20.00 ml of the sodium oxalate solution?

42. A sample of $Na_2C_2O_4$ weighing 1.6260 g is dissolved in water in a 250-ml measuring flask. What quantity, in ml, of a $0.09768N$ solution of $KMnO_4$ will be spent for the titration of 25.00 ml of the sodium oxalate solution?

43. A sample of $H_2C_2O_4 \cdot 2H_2O$ weighing 0.7564 g is dissolved in water in a 250-ml volumetric flask. What quantity, in ml, of a $KMnO_4$ solution ($T_{KMnO_4} = 0.001616$) will be spent for the titration of 25.00 ml of the oxalic acid?

44. A sample of $H_2C_2O_4 \cdot 2H_2O$ weighing 1.6540 g is dissolved in water in a 200-ml volumetric flask. What quantity, in ml, of a $KMnO_4$ solution ($T_{KMnO_4/Fe} = 0.005616$)

will be spent for the titration of 20.00 ml of the oxalic acid solution?

45. What quantity, in ml, of a 0.1054*N* solution of $KMnO_4$ will be used for the titration of 0.1600 g of $(NH_4)_2C_2O_4 \cdot H_2O$ dissolved in 25.00 ml of water? Will the amount of a $KMnO_4$ solution required to titrate the same sample dissolved in a different volume of water be different?

46. What amount, in ml, of a $KMnO_4$ solution (K = = 1.2140 for 0.2*N*) will be spent for the titration of a solution obtained by dissolving 0.1324 g of $Na_2C_2O_4$ in an arbitrary volume of water?

47. What quantity, in ml, of a 0.1112*N* $KMnO_4$ solution will be used in the titration of 0.1612 g of $Na_2C_2O_4$ dissolved in an arbitrary amount of water?

48. What quantity, in ml, of a $KMnO_4$ solution (T_{KMnO_4} = = 0.001562) will be spent for the titration of a solution obtained by dissolving 0.7580 g of $H_2C_2O_4 \cdot 2H_2O$ in an arbitrary volume of water?

Calculating the Mass of a Sample

49. Calculate the mass of a sample of commercial green vitriol in order to determine the $FeSO_4$ by the permanganate method, if the concentration of the standard solution of $KMnO_4$ is about 0.1*N* and the capacity of the volumetric flask in which the sample is to be dissolved is 250 ml.

50. Determine the mass of a sample of commercial sodium oxalate to be used in testing for $Na_2C_2O_4$, if the concentration of the standard solution of $KMnO_4$ is about 0.05*N* and the capacity of the volumetric flask is 250 ml.

51. Determine the mass of a sample of commercial crystalline oxalic acid to be used in testing for $H_2C_2O_4 \cdot 2H_2O$, if an approximately 0.1*N* $KMnO_4$ solution is used for the titration and the capacity of the volumetric flask is 500 ml.

52. Calculate the mass of a sample of commercial ammonium oxalate monohydrate to be used in testing for purity, if K of the standard solution of $KMnO_4$ is 1.042 for 0.1*N*, and the capacity of the volumetric flask is 500 ml.

53. Determine the mass of a sample of an alloy to be used in testing for iron by the permanganate method, if the

sample is dissolved, reduced, the solution diluted to 250 ml, the concentration of $KMnO_4$ solution is 0.1*N*, and the Fe content of the alloy is about 20 per cent.

54. A sample of commercial sodium sulphite contains about 45 per cent of Na_2SO_3. What should the mass of the sample be if the capacity of the volumetric flask used for preparing the solution is 200 ml and the sample is tested for purity with an approximately 0.05*N* solution of $KMnO_4$?

55. Calculate the mass of a sample of commercial oxalic acid containing about 70 per cent of $H_2C_2O_4$ to be used in testing for purity by the method of separate samples, using an approximately 0.2*N* solution of $KMnO_4$ and a 50-ml burette.

Note: As a rule, for the method of separate samples, the mass of a sample is calculated so that about half the volume of the burette will be used in titration with potassium permanganate.

56. Calculate the mass of a sample of slag containing about 5 per cent of Fe if it is to be used in testing for FeO by the permanganate method of separate samples, when the concentration of the $KMnO_4$ solution is about 0.1*N* and the capacity of the burette is 25 ml.

57. Determine the mass of a sample of commercial green vitriol containing about 15 per cent of $FeSO_4$ if it is to be used for the determination of $FeSO_4$ in the sample by the method of separate samples, when a 0.05*N* solution of $KMnO_4$ is used for titration and the capacity of the burrette is 50 ml.

58. Calculate the mass of a sample of iron ore to be used for testing for Fe by the permanganate method of separate samples, if the concentration of the $KMnO_4$ solution is about 0.2*N*, the capacity of the burette is 50 ml, and the anticipated Fe content of the sample is about 40 per cent.

Calculating the Results by Direct Titration Data

59. A sample of oxalic acid is dissolved in a 250-ml volumetric flask. To titrate 25.00 ml of the solution we use 24.30 ml of $KMnO_4$ ($K = 1.0142$ for 0.05*N*). Determine the quantity, in grams, of $H_2C_2O_4 \cdot 2H_2O$ in the sample.

60. A solution of ammonium oxalate is diluted with water in a 200-ml volumetric flask. To titrate 20.00 ml of this solution we use 19.85 ml of a $KMnO_4$ solution (K = 0.8960 for 0.10N). What quantity, in grams, of $(NH_4)_2C_2O_4 \cdot H_2O$ is contained in the solution?

61. A solution of oxalic acid is prepared in a 200-ml volumetric flask. If 20.00 ml of the solution are titrated with 18.25 ml of a $KMnO_4$ solution (T_{KMnO_4} = 0.001616), what quantity, in grams, of anhydrous $H_2C_2O_4$ is contained in the solution?

62. A sample of sodium oxalate is dissolved in a 500-ml volumetric flask. If 21.40 ml of a $KMnO_4$ solution (T_{KMnO_4} = 0.005751) are spent for the titration of 20 ml of the oxalate solution, what quantity, in grams, of $Na_2C_2O_4$ is contained in the sample?

63. To titrate a solution of $(NH_4)_2C_2O_4 \cdot H_2O$ we use 25.80 ml of a $KMnO_4$ solution ($T_{KMnO_4/Fe}$ = 0.005585). What quantity, in grams, of $(NH_4)_2C_2O_4 \cdot H_2O$ is contained in the solution?

64. In order to determine iron in 20 ml of a solution obtained by dissolving a sample of a metal alloy 41.50 ml of a $KMnO_4$ solution ($T_{KMnO_4/Fe}$ = 0.002980) are used in titration. What quantity, in grams, of iron is contained in the sample? Will the result change if the same sample is dissolved in a different volume?

65. To titrate a solution of ammonium oxalate, we use 28.15 ml of a $KMnO_4$ solution (T = 0.003218). What quantity, in grams, of $(NH_4)_2C_2O_4 \cdot H_2O$ is contained in the sample?

66 To titrate a solution of $FeSO_4$ we use 21.60 ml of a $KMnO_4$ solution (T = 0.002852). What quantity, in grams, of $FeSO_4$ is contained in the solution?

67. A sample of iron ore is dissolved, reduced, and titrated with 42.35 ml of a $KMnO_4$ solution (T_{KMnO_4} = 0.001842). What quantity, in grams, of Fe_2O_3 is contained in the sample?

68. A sample of iron wire is dissolved, in the absence of air, in sulphuric acid and titrated with 35.40 ml of a $KMnO_4$ solution (T_{KMnO_4} = 0.003082). What quantity, in grams, of iron is contained in the sample?

69. What quantity, in grams, of iron is contained in a solution, if 26.65 ml of a $KMnO_4$ solution ($T_{KMnO_4/Fe}$ = = 0.003040) are spent for its titration?

70. What quantity, in grams, of $H_2C_2O_4 \cdot 2H_2O$ is contained in a solution, if 26.75 ml of a $KMnO_4$ solution ($T_{KMnO_4/Fe} = 0.01122$) are spent for its titration?

71. What quantity, in grams, of Fe_2O_3 is contained in an iron ore sample, if 32.88 ml of a $KMnO_4$ solution ($T_{KMnO_4/FeSO_4} = 0.01519$) are spent for the titration of the solution obtained by dissolving the sample and after its subsequent reduction?

72. If 21.30 ml of a $KMnO_4$ solution ($K = 0.9820$ for $0.2N$) are spent for the titration of a sodium oxalate solution, what quantity, in grams, of $Na_2C_2O_4$ is contained in the solution?

73. A sample of ammonium oxalate weighing 1.9710 g is dissolved in a 500-ml volumetric flask. To titrate this solution, 28.25 ml of a $KMnO_4$ solution are used. Calculate the percentage of $(NH_4)_2C_2O_4 \cdot H_2O$ in the sample if $K_{KMnO_4} = 0.9530$ for $0.05N$.

74. A piece of iron wire weighing 1.0130 g is dissolved, in the absence of air, in hydrochloric acid. The solution is diluted with water in a 250-ml volumetric flask to the mark. Calculate the percentage of Fe in the sample, if K_{KMnO_4} is 1.0050 for $0.1N$, the volume of the test solution is 25.00 ml, and the amount of $KMnO_4$ solution spent for titration is 17.81 ml.

75. Calculate the percentage of $H_2C_2O_4 \cdot 2H_2O$ in a sample weighing 3.3900 g if it is dissolved in a 500-ml volumetric flask and 23.52 ml of a $0.1124N$ solution of $KMnO_4$ are spent to titrate 25.00 ml of the solution.

76. A sample of commercial green vitriol weighing 7.1500 g is dissolved in a 250-ml volumetric flask. To titrate 25.00 ml of the resultant solution, 24.48 ml of a $0.0986N$ $KMnO_4$ solution are used. Calculate the percentage of $FeSO_4 \cdot 7H_2O$ in the sample.

77. A sample of iron ore weighing 1.7950 g is dissolved and reduced, the solution is diluted in a 250-ml volumetric flask, and 20.00 ml of the resultant solution are titrated with 18.65 ml of a $KMnO_4$ solution ($T = 0.001842$). Calculate the percentage of Fe in the sample.

78. A sample of commercial green vitriol weighing 15.9900 g is dissolved in a 500-ml volumetric flask. To titrate 25.00 ml of the solution 27.80 ml of a $KMnO_4$ solution

(T = 0.003218) are used. Calculate the percentage of $FeSO_4 \cdot 7H_2O$ in the sample.

79. A sample of commercial sodium sulphite weighing 2.6770 g is dissolved in a 200-ml measuring flask. If 20.00 ml of the solution are titrated with 19.20 ml of a $KMnO_4$ solution, calculate the percentage of (a) Na_2SO_3 and (b) $Na_2SO_3 \cdot 7H_2O$, if $T_{KMnO_4/Fe}$ is 0.005585.

80. The following data are obtained during the testing of iron chloride for $FeCl_2 \cdot 4H_2O$: the mass of the sample, 0.2658 g; $T_{KMnO_4/FeO} = 0.003620$; the amount of $KMnO_4$ solution spent for titration, 23.48 ml. Calculate the percentage of $FeCl_2 \cdot 4H_2O$ in the sample.

81. A sample of hydrogen peroxide weighing 5.0000 g is dissolved with water in a 500-ml volumetric flask. To titrate 25.00 ml of this solution 37.43 ml of a $KMnO_4$ solution are used. Calculate the percentage of H_2O_2 in the sample, if K_{KMnO_4} is 1.1240 for 0.1*N*.

82. A sample of hydrogen peroxide weighing 1.1500 g is dissolved with water in a 250-ml volumetric flask. To titrate 25.00 ml of the solution 30.25 ml of a $KMnO_4$ solution ($T_{KMnO_4/O} = 0.0004642$) are used. Calculate the percentage of oxidizing oxygen in the sample.

83. A sample of commercial sodium nitrite weighing 1.3730 g is dissolved in water in a 1000-ml volumetric flask. The solution is used to titrate 20.00 ml of $KMnO_4$ solution in wihch $K = 0.9870$ for 0.05*N*. If 26.90 ml of the test solution are used in the titration, calculate the percentage of $NaNO_2$ in the sample.

84. A sample of sodium nitrite weighing 0.9457 g is dissolved in a 200-ml volumetric flask. To titrate 20.00 ml of a $KMnO_4$ solution, in which T_{KMnO_4/Fe_2O_3} is 0.007985, 16.85 ml of the nitrite solution are used. Calculate the percentage of $NaNO_2$ in the sample.

85. A sample of commercial green vitriol weighing 0.7220 g is dissolved in water and its entire quantity titrated with 23.20 ml of potassium permanganate with the titre of 0.003161. Calculate the percentage of $FeSO_4 \cdot 7H_2O$.

86. A sample of piano wire weighing 0.0689 g is dissolved, in the absence of air, in sulphuric acid and titrated with 24.55 ml of potassium permanganate (T = 0.001565). Calculate the percentage of Fe in the sample.

87. A sample of oxalic acid weighing 0.3745 g is dissolved and titrated with 38.42 ml of potassium permanganate ($T_{KMnO_4/Fe}$ = 0.007982). Calculate the percentage of $H_2C_2O_4 \cdot 2H_2O$ in the sample.

88. A sample of ammonium oxalate weighing 0.1485 g is tested for purity. The sample is dissolved and its entire solution titrated with 28.90 ml of potassium permanganate ($T_{KMnO_4/(NH_4)_2C_2O_4 \cdot H_2O}$ = 0.004308). What quantity, in per cent, of $(NH_4)_2C_2O_4 \cdot H_2O$ is contained in the sample?

89. A sample of iron ore weighing 0.1709 g is dissolved and reduced. The obtained solution is titrated with 38.42 ml of a 0.0505*N* solution of $KMnO_4$. Calculate the percentage of Fe_2O_3 in the sample.

90. A solution of 0.2343 g of sodium sulphite is titrated with 34.50 ml of a $KMnO_4$ solution (K = 0.9832 for 0.05*N*). Calculate the percentage of anhydrous Na_2SO_3 in the sample.

Back Titration. In this method two standard solutions readily react with each other (for example, oxidant and reductant, acid and alkali). If the desired substance is an oxidant, it can be treated with an accurately measured quantity of pure reducing agent, so that part of it reacts with the desired oxidant and part remains in excess. The amount of this excess is determined by titration with the other standard solution, an oxidant. The quantity of the reducing agent titrated with the second standard solution is subtracted from the original quantity of the reductant. The difference is equivalent to the quantity of the desired oxidant. For example, in the analysis of pyrolusite, a sample is treated with a definite (but necessarily excessive) quantity of oxalate. As soon as the entire manganese dioxide contained in the sample has reacted, the excess oxalate is titrated with a solution of potassium permanganate.

The second standard substance is always in solution form; the first can be a dry substance or its solution, whose volume is accurately measured. In the former case the calculations are performed basically as follows:

Let x and E_x be the quantity and equivalent weight of the oxidant to be determined; m_1 and E_{st}, the quantity and equivalent weight of the standard reducing agent; m_2, the quantity of titrated excess of the reducing agent. Then, $(m_1 - m_2)$ is the quantity of the first standard substance, which is equiv-

alent to the quantity of the determined oxidant. Therefore

$$\begin{array}{l} E_x - E_{st} \\ \\ x - (m_1 - m_2) \end{array} \qquad x = \frac{E_x (m_1 - m_2)}{E_{st}} \text{ g.}$$

The percentage of the desired component can be calculated when required.

Example 1. To determine the MnO_2 content of a pyrolusite sample weighing 0.2962 g, it is placed in a solution prepared from 0.3985 g of pure $H_2C_2O_4 \cdot 2H_2O$ and also containing H_2SO_4. On completion of the reaction, the solution is titrated with 18.25 ml of a potassium permanganate solution ($K = 1.1050$ for $0.01N$). Calculate the percentage of MnO_2 in the sample.

Solution. First determine the quantity of $H_2C_2O_4 \cdot 2H_2O$ titrated with potassium permanganate, i.e. the quantity of $KMnO_4$ that remained in excess after the reaction with MnO_2. Since 18.25 ml of $KMnO_4$ ($K = 1.1050$ for $0.01N$) reacts with the same volume of oxalic acid of the same normality, the quantity of the titrated $H_2C_2O_4 \cdot 2H_2O$ will be

$$m_2 = \frac{1.1050 \times 0.01 \times 63.03 \times 18.25}{1000} = 0.01271 \text{ g.}$$

Next we find what quantity of $H_2C_2O_4 \cdot 2H_2O$ has reacted with MnO_2:

$$m_1 - m_2 = 0.3985 - 0.01271 = 0.3858 \text{ g.}$$

We now find the quantity of MnO_2 with which the quantity of oxalic acid has reacted:

$$\begin{array}{l} E_{H_2C_2O_4 \cdot 2H_2O} - E_{MnO_2} \\ \\ 63.03 - 43.47 \\ \\ 0.3858 - x \end{array} \qquad x = \frac{0.3858 \times 43.47}{63.03} \text{ g.}$$

Hence, the percentage of MnO_2 in the sample is

$$\frac{0.3858 \times 43.47 \times 100}{63.03 \times 0.2962} = 89.83 \text{ per cent.}$$

In the second case the quantities of both standard substances are expressed by the volumes of standard solutions used. The result is then calculated by reducing them to the same normality, as described on page 134.

Example 2. A sample of pyrolusite weighing 0.2462 g is treated with 50 ml of oxalate ($K = 1.2460$ for $0.1N$) in an acid medium. The amount of a potassium permanganate solution ($K = 0.9260$ for $0.05N$) spent for the titration of the excess of the oxalate solution is 42.48 ml. Determine the MnO_2 content of the sample.

Solution. Adjust the volumes of both solutions to $1N$ concentration and determine, by subtraction, the quantity of oxalate which has reacted with the MnO_2:

$$50.00 \times 1.2460 \times 0.1 = 6.230 \text{ ml of } 1N \text{ oxalate (or 6.230 mg-equiv)}$$

$$-$$

$$42.48 \times 0.9260 \times 0.05 = 1.967 \text{ ml of } 1N \text{ oxalate (or 1.967 mg-equiv)}$$

$$4.263 \text{ ml of } 1N \text{ oxalate (or 4.263 mg-equiv)}$$

Hence, the MnO_2 has reacted with the amount of oxalate which is contained in 4.263 ml of a $1N$ solution or, the same thing, 4.263 mg-equivalents of oxalate, which have reacted with the same number of milligram-equivalents of MnO_2. Therefore, to find the MnO_2 content of the sample it is necessary to multiply the calculated difference by a milligram-equivalent of MnO_2:

$$4.263 \times \frac{43.47}{1000} = a \text{ g.}$$

Now find the percentage:

$$\frac{a \times 100}{\text{sample}} = \frac{4.263 \times 43.47 \times 100}{1000 \times 0.2462} = 75.27 \text{ per cent.}$$

The quantity of reducing agent required to treat a desired oxidant should be calculated in three steps:

(1) the quantity of reducing agent required for the reaction with the oxidant contained in the sample is first determined;

(2) next we determine the excess quantity of the reductant, which is titrated with about half the burette volume of a standard solution of potassium permanganate;

(3) finally the found quantities are added together.

Example 3. What quantity, in grams, of $(NH_4)_2C_2O_4 \cdot H_2O$ should be taken to treat 0.5 g of commercial MnO_2 of about 75 per cent purity, if a 200-ml volumetric flask, a 50-ml pipette, and an approximately 0.1*N* $KMnO_4$ solution are used in the analysis?

Solution. Find the MnO_2 content of the sample:

$$\frac{0.5 \times 75}{100} \simeq 0.4 \text{ g}.$$

Next determine the quantity of the oxalate which will react with 0.4 g of MnO_2

$$\begin{array}{c} E_{MnO_2} - E_{ox} \\ 43.5 - 71 \text{ g} \\ 0.4 - x \text{ g} \end{array} \qquad x \simeq \frac{0.4 \times 71}{44} \simeq 0.65 \text{ g}.$$

Also find the mass of oxalate which would have a concentration of 0.1*N* in a 200 ml-volumetric flask:

$$\frac{71 \times 0.1 \times 200}{1000} \simeq 1.4 \text{ g}.$$

Hence, the quantity of oxalate required to treat the sample is

$$0.65 + 1.4 = 2.05 \text{ g of oxalate}.$$

Example 4. What quantity, in grams, of ammonium oxalate is required to treat 0.1 g of 75 per cent pyrolusite if it is tested for purity by the method of separate samples with a 0.1*N* $KMnO_4$ solution using a 50-ml burette?

Solution. As in the previous example, find the approximate MnO_2 content of the sample:

$$\frac{0.1 \times 75}{100} = 0.075 \text{ g}.$$

This quantity of MnO_2 will react with

$$\frac{0.075 \times 71}{44} = 0.12 \text{ g of oxalate}.$$

Since about 25 ml (half the burette capacity) of a 0.1*N* $KMnO_4$ solution will be spent for the titration of excess oxalate, this excess will be

$$\frac{71 \times 0.1 \times 25}{1000} \simeq 0.18 \text{ g}.$$

The required amount of oxalate will therefore be 0.12 + + 0.18 = 0.3 g.

91. A sample of pyrolusite weighing 0.4 g was taken for the determination of MnO_2. What quantity, in grams, of $(NH_4)_2C_2O_4 \cdot H_2O$ is required to dissolve the sample if a 250-ml volumetric flask, a 25-ml pipette, and a 0.1*N* standard solution of $KMnO_4$ are used for the back titration of excess oxalate? The MnO_2 content of the sample is about 75 per cent.

92. Solve Problem 91 taking a sample weighing 0.2 g (instead of 0.4 g), all other conditions being the same.

93. What quantity, in grams, of crystalline ammonium oxalate is required to dissolve and treat 0.3 g of pyrolusite containing about 60 per cent of MnO_2. The analysis is aimed at determining the MnO_2 and the pipetting method is used. The capacity of the volumetric flask is 200 ml, of the pipette 20 ml, and the concentration of the $KMnO_4$ solution is 0.05*N*.

94. A sample of pyrolusite containing about 80 per cent of MnO_2 and weighing 0.5 g is analysed for the determination of the MnO_2 content. What quantity, in grams, of crystalline oxalic acid should be taken to treat the sample, if the capacity of the volumetric flask is 500 ml, of a pipette 25 ml, and the concentration of a $KMnO_4$ solution is 0.2*N*?

95. What quantity, in ml, of oxalic acid is required to treat 0.2 g of pyrolusite in an analysis of MnO_2 content, if the capacity of the volumetric flask is 200 ml, of the pipette 20 ml, and the titre of the standard $KMnO_4$ solution is 0.00316? The MnO_2 content of the sample is about 75 per cent.

96. Solve Problem 95 using $H_2C_2O_4 \cdot 2H_2O$ with the titre of 0.0063 and a 0.05*N* $KMnO_4$ solution, the other conditions being the same.

97. Calculate the mass of pure crystalline ammonium oxalate in order to treat 0.1 g of commercial MnO_2 in testing for the MnO_2 content by the method of separate samples, if the capacity of the burette is 50 ml, the concentration of $KMnO_4$ is about 0.1*N* and the MnO_2 content of the sample is about 90 per cent.

98. A sample of pyrolusite weighing 0.2 g contains about 80 per cent of MnO_2. What quantity, in grams, of pure crys-

talline ammonium oxalate is required to treat this sample so that about 25 ml of a standard $KMnO_4$ solution (K = = 0.900 for 0.05N) will be spent for the titration of excess $(NH_4)_2C_2O_4$?

99. To dissolve 0.15 g of pyrolusite containing about 70 per cent of MnO_2 50 ml of a 0.1N solution of $H_2C_2O_4$ are used. Will the capacity of a 50-ml burette be sufficient for the titration of excess oxalic acid with a $KMnO_4$ solution if T_{KMnO_4} is 0.0031?

100. To dissolve 0.1 g of MnO_2 0.2 g of crystalline ammonium oxalate is used. What is the colour of the solution after adding the first drops of a standard $KMnO_4$ solution?

101. A sample of pyrolusite weighing 0.3812 g is treated with 0.4220 g of $H_2C_2O_4 \cdot 2H_2O$. To titrate the unreacted excess of oxalic acid 15.05 ml of a $KMnO_4$ solution (K = = 0.9850 for 0.1N) are used. Calculate the percentage of MnO_2 in the sample.

102. A sample of pyrolusite was tested for the MnO_2 content. The following data were obtained: the sample mass, 0.4012 g; the mass of $Na_2C_2O_4$, 0.4488 g; the amount of a $KMnO_4$ solution spent for titration, 30.20 ml; K_{KMnO_4} = = 1.0120 for 0.05N. Calculate the percentage of MnO_2 in the sample.

103. A sample of pyrolusite weighing 0.4036 g is treated with 50.00 ml of an oxalic acid solution (K = 0.9750 for 0.1N). Excess unreacted acid was back titrated with 15.90 ml of a $KMnO_4$ solution (K = 1.125 for 0.1N). Calculate the percentage of MnO_2 in the sample.

104. A sample of potassium chlorate weighing 0.1510 g is dissolved and treated with 100.00 ml of a 0.09852N solution of $Na_2C_2O_4$. To titrate excess sodium oxalate 48.60 ml of a $KMnO_4$ solution (K = 1.0640 for 0.05N) were used. Calculate the percentage of $KClO_3$ in the sample.

105. A sample of potassium chlorate weighing 2.1510 g was dissolved in a 250-ml volumetric flask. Calculate the percentage of $KClO_3$ in the sample, if 25.00 ml of the obtained solution were treated with 45.00 ml of Mohr's salt solution (K = 1.3200 for 0.1N) and 17.50 ml of a $KMnO_4$ solution (K = 1.2000 for 0.1N) were used to titrate the excess salt solution.

106. A sample of pyrolusite weighing 0.3264 g was treated

with sulphuric acid and 3.0527 g of $H_2C_2O_4 \cdot 2H_2O$. The resultant solution was transferred quantitatively into a 250-ml volumetric flask and water was added to the mark. The amount of a $KMnO_4$ solution ($K = 1.122$ for $0.2N$) required to titrate 25.00 ml of the solution obtained is 19.20 ml. Calculate the percentage of MnO_2 in the sample.

107. A sample of marble weighing 0.7324 g is dissolved and then treated with 1.4960 g of $(NH_4)_2C_2O_4 \cdot H_2O$. The solution is neutralized in a 200-ml flask and water is added to the mark. To titrate 25.00 ml of the filtered solution 19.90 ml of a $KMnO_4$ solution ($K = 0.8564$ for $0.05N$) are spent. Calculate the percentage of CaO in the sample.

108. A sample of calcite weighing 0.5890 g was tested for $CaCO_3$ content. The mass of $Na_2C_2O_4$ was 1.3470 g; the capacity of the volumetric flask, 250 ml; the amount of the solution to be titrated, 25.00 ml; the amount of a $KMnO_4$ olution spent for titration, 17.20 ml; $K_{KMnO_4} = 0.9710$ for $0.05N$. Calculate the percentage of $CaCO_3$ in the sample.

109. A sample of limestone weighing 0.8010 g was dissolved and treated with ammonium oxalate. The precipitate of CaC_2O_4 was washed and dissolved in H_2SO_4. The solution was diluted in a 250-ml volumetric flask and water added to the mark. The amount of a $0.1230N$ $KMnO_4$ solution spent for titration of 25.00 ml of the solution was, on the average, 10.38 ml. Calculate the percentage of $CaCO_3$ in the sample.

110. A sample of limestone weighing 0.1627 g is dissolved and then treated with an excess quantity of ammonium oxalate. The precipitate is washed and treated with H_2SO_4. The solution obtained is titrated quantitatively with a $KMnO_4$ solution. The amount of the $KMnO_4$ solution spent for titration is 31.42 ml ($T = 0.00293$). Determine the percentage of CaO in the limestone sample.

C. Iodometry

Calculations are similar for all titrimetric methods of analysis, differing only in the values of gram-equivalents of reagents used. Thus all calculations in iodometry are the same as in permanganatometric determinations.

Problems

Calculating the Mass of Reagents Used in the Preparation of Standard Solutions

1. What quantity, in grams, of pure iodine is required to prepare 250 ml of an approximately 0.05*N* solution?

2. What quantity, in grams, of pure iodine is required to prepare 500 ml of an approximately 0.1*N* solution?

3. What quantity, in grams, of crystalline sodium thiosulphate is required to prepare 1.5 litres of an approximately 0.1*N* solution?

4. What quantity, in grams, of crystalline sodium thiosulphate is required to prepare 800 ml of an approximately 0.05*N* solution?

5. What quantity, in grams, of pure potassium dichromate is required to prepare 500 ml of a solution used for the standardization of an approximately 0.1*N* solution of $Na_2S_2O_3$?

6. What quantity, in grams, of pure potassium dichromate should be taken to prepare 200 ml of an approximately 0.1*N* solution?

7. Calculate the mass of pure $K_2Cr_2O_7$ required to standardize an approximately 0.05*N* solution of $Na_2S_2O_3$ by the method of separate samples, if about 25 ml of the $Na_2S_2O_3$ solution are required to titrate the $K_2Cr_2O_7$ solution.

8. What quantity, in grams, of pure $K_2Cr_2O_7$ should be taken to standardize an approximately 0.05*N* solution of $Na_2S_2O_3$ by the method of separate samples using a 50-ml burette?

9. To standardize an approximately 0.1*N* solution of $Na_2S_2O_3$ we take 0.1238 g of pure $K_2Cr_2O_7$. Can this sample be used if the capacity of the burette is 25 ml?

10. To standardize an approximately 0.1*N* solution of $Na_2S_2O_3$ by the method of separate samples, a sample of pure $K_2Cr_2O_7$ weighing 0.1190 g is used. Is the capacity of a 50-ml burette sufficient for titration?

11. To 20.00 ml of an iodine solution ($K = 1.0860$ for 0.1*N*) added are 45.00 ml of a sodium thiosulphate solution ($K = 0.9862$ for 0.05*N*). Next, 1 ml of a starch solution is added. Will the solution be blue in colour?

12. To a solution obtained by dissolving 0.1432 g of pure $K_2Cr_2O_7$ we add an acid, potassium iodide, starch, and 25.00 ml of sodium thiosulphate (K = 1.1010 for 0.1N). Will the solution turn colourless?

Standardization of Sodium Thiosulphate Solutions

13. A sample of sublimed iodine weighing 0.6300 g is dissolved in a 500-ml volumetric flask. Determine the titre of the solution.

14. A sample of pure iodine weighing 1.2620 g is dissolved in a 250-ml volumetric flask. Determine the titre of the solution.

15. A sample of pure iodine weighing 2.9840 g is dissolved in a 500-ml volumetric flask. Determine the normality of the solution.

16. A sample of pure iodine weighing 6.3250 g is dissolved in a 1000-ml volumetric flask. Determine the normality and titre of the solution against $Na_2S_2O_3 \cdot 5H_2O$.

17. During the standardization of a sodium thiosulphate solution, 1.1780 g of pure $K_2Cr_2O_7$ were dissolved in a 250-ml volumetric flask. The amount of the sodium thiosulphate solution spent for titration of 25.00 ml of the prepared solution (after the relevant treatment) was 23.38 ml. What is the normality and K of the sodium thiosulphate solution?

18. During the standardization of a sodium thiosulphate solution, 0.2486 g of pure $K_2Cr_2O_7$ was dissolved in a 500-ml volumetric flask. HCl and KI were then added to the solution, and 25.00 ml of it were titrated with an average of 25.05 ml of the sodium thiosulphate solution. Determine the normality and titre of the sodium thiosulphate solution.

19. A sample of pure $K_2Cr_2O_7$ weighing 0.1180 g is treated with potassium iodide in an acid medium and titrated with 23.80 ml of a sodium thiosulphate solution. What is the titre of the thiosulphate solution?

20. To titrate the iodine isolated from an iodide solution by 0.1154 g of potassium dichromate 23.74 ml of a sodium thiousulphate solution are used. Determine the following: (a) $T_{Na_2S_2O_3 \cdot 5H_2O}$; (b) $T_{Na_2S_2O_3 \cdot 5H_2O/I}$.

21. If KI and HCl are added to 20.00 ml of a $KMnO_4$ soluton (K = 1.056 for 0.1N) and the resultant solution is

titrated with 18.50 ml of a sodium thiosulphate solution, determine the following: (a) T; (b) N; (c) K of the sodium thiosulphate solution

22. Iodine liberated from potassium iodide by 12.50 ml of a $KMnO_4$ solution (T = 0.001544) is titrated with 17.05 ml of a $Na_2S_2O_3$ solution. Determine the following: (a) T; (b) N; (c) K of the sodium thiosulphate solu ion.

Calculating the Mass of a Sample

23. Calculate the mass of a sample of lime chloride containing about 25 per cent of active chlorine for a purity test, if the sample is dissolved in a 500-ml volumetric flask and the concentration of a sfandard solution of sodium thiosulphate is about $0.2N$.

24. Determine the mass of a sample of sodium bichromate for a purity test, if the sample contains about 15 per cent of moisture and about 5 per cent of insoluble admixtures. The capacity of the volumetric flask used for dissolving the sample is 250 ml and the concentration of a standard solution of sodium thiosulphate is about $0.1N$.

25. What is the maximum possible mass of a sample of lime chloride for the analysis for active chlorine content by the method of separate samples, if the expected content of active chlorine in the sample is about 20 per cent, the concentration of a sodium thiosulphate solution is about $0.1N$, and the amount of the sodium thiosulphate solution to be spent for titration does not exceed 40 ml?

26. Calculate the mass of a sample of iodine containing about 20 per cent of impurities having no oxidizing properties, if a maximum of 25 ml of a $0.05N$ $Na_2S_2O_3$ solution is spent for the titration of the solution obtained.

27. What quantity, in ml, of a hydrogen peroxide solution prepared by diluting 25 ml of a 3 per cent solution to 250 ml should be taken, so that after treatment of the dilute solution with KI and HCl about 25 ml of an approximately $0.15N$ $Na_2S_2O_3$ solution will be spent for its titration?

28. What quantity, in ml, of chlorine water containing about 2 per cent of chlorine is required so that about 30 ml of a sodium thiosulphate solution ($T_{Na_2S_2O_3 \cdot 5H_2O}$ = = 0.02500) will be spent for its titration after the appropriate treatment?

Calculating the Results by Direct Titration Data

29. A sample of sodium thiosulphate weighing 15.9800 g was dissolved in a 500-ml volumetric flask to test for purity. To titrate 25.00 ml 30.60 ml of a standard iodine solution ($K = 0.9780$ for $0.1N$) were used. Calculate the percentage of $Na_2S_2O_3 \cdot 5H_2O$ in the sample.

30. A sample of sodium sulphide weighing 0.9432 g was dissolved in a 200-ml volumetric flask. To titrate 20.00 ml of this solution 15.42 ml of a standard solution of iodine ($K = 1.2040$ for $0.1N$) were used. Calculate the percentage of Na_2S in the sample.

31. A sample of sodium sulphite weighing 7.3460 g was dissolved in a 1000-ml volumetric flask. The solution thus obtained was used to titrate 20.00 ml of an iodine solution ($N = 0.05140$). The amount of the sodium sulphite solution spent for titration was 23.15 ml. Calculate the percentage of Na_2SO_3 in the sample.

32. A sample of sodium thiosulphate weighing 1.4460 g was dissolved in a 500-ml volumetric flask. The solution was used to titrate 20.00 ml of an iodine solution ($K = 1.0250$ for $0.01N$). The amount of the solution spent for titration was 18.95 ml. Calculate the percentage of $Na_2S_2O_3 \cdot 5H_2O$ in the sample.

33. A sample of ferric chloride weighing 4.8900 g was dissolved in a 250-ml volumetric flask, and 25.00 ml of the solution was treated with potassium iodide in an acid medium and titrated with a sodium thiosulphate solution ($K = 0.9230$ for $0.1N$). The amount of the solution spent for titration was 32.10 ml. Calculate the percentage of $FeCl_3$ in the sample.

34. A sample of iodine containing insoluble impurities and weighing 1.6220 g was dissolved in a 250-ml volumetric flask. To titrate 25.00 ml of the solution obtained, 19.95 ml of a sodium thiosulphate solution were used ($K = 1.0500$ for $0.05N$). Calculate the percentage of iodine in the sample.

35. A sample of lime chloride weighing 3.3580 g was diluted in a 250-ml volumetric flask. To titrate 25.00 ml of the suspension, after the addition of HCl and KI 17.74 ml of a sodium thiosulphate solution ($K = 0.9882$ for $0.1N$) were used. Calculate the percentage of active chlorine in the sample.

36. A sample of lime chloride weighing 3.3590 g was diluted in a 250-ml volumetric flask. To titrate 25.00 ml of the suspension, after the appropriate treatment 18.29 ml of a sodium thiosulphate solution (T = 0.02453) were used. Calculate the percentage of active chlorine in the sample.

37. A sample of sodium sulphite weighing 0.3595 g was dissolved in an arbitrary amount of water. The solution was titrated with 28.65 ml of a standard iodine solution (T = = 0.01142). Calculate the percentage of $Na_2SO_3 \cdot 7H_2O$ in the sample.

38. A sample of sodium sulphide weighing 0.0902 g was dissolved in an arbitrary amount of water. The solution was titrated with 18.20 ml of an iodine solution. Calculate the percentage of Na_2S in the sample, if the titre of the iodine solution is 0.01320.

39. A sample of lime chloride weighing 0.2608 g was treated with KI and HCl and then titrated with 25.95 ml of a sodium thiosulphate solution (K = 1.0020 for 0.1N). Calculate the percentage of active chlorine in the sample.

40. A sample of potassium bichromate weighing 0.1254 g was dissolved in an arbitrary amount of water and iodine, liberated by this solution from potassium iodide, was titrated with 24.85 ml of a sodium thiosulphate solution (K = = 0.9978 for 0.1N). Calculate the percentage of CrO_3 in the sample.

41. A sample of commercial hypochlorite weighing 0.2110 g was dissolved and iodine, liberated from the solution, was titrated with 19.50 ml of a sodium thiosulphate solution ($T_{Na_2S_2O_3/I}$ = 0.01273). Calculate the percentage of chlorine in the sample.

42. To titrate 25.00 ml of a potassium iodate solution, which has been added to a solution of KI and HCl, 26.55 ml of a sodium thiosulphate solution ($T_{Na_2S_2O_3/K_2Cr_2O_7}$ = = 0.004875) are used. What is T_{KIO_3}?

43. To titrate iodine, liberated from an acid solution of potassium iodide by 0.3000 g of potassium iodate, 48.00 ml of a $Na_2S_2O_3$ solution are used. Determine the following: (a) $T_{Na_2S_2O_3/I}$; (b) the normality of the sodium thiosulphate solution.

44. A sample of potassium iodide weighing 4.3780 g is dissolved in a 200-ml volumetric flask. To titrate 20.00 ml

of this solution after treatment with an oxidant 23.16 ml of a sodium thiosulphate solution ($T_{Na_2S_2O_3/K_2Cr_2O_7}$ = = 0.005248) a e used. Calculate the percentage of KI in the sample.

45. A sample of chromic acid anhydride weighing 0.0921 g is dissolved, treated with KI and HCl, and titrated with 23.75 ml of sodium thiosulphate solution ($T_{Na_2S_2O_3/I}$ = = 0.01354). Calculate the percentage of CrO_3 in the sample.

46. To titrate 0.3319 g of hypochlorite after dissolution and the appropriate treatment 30.19 ml of a sodium thiosulphate solution ($T_{Na_2S_2O_3 \cdot 5H_2O}$ = 0.02512) are used. Calculate the percentage of chlorine in the sample.

Calculating the Results by Back Titration Data

47. A sample of sodium sulphide weighing 3.9050 g was dissolved in a 500-ml volumetric flask. To 20.00 ml of the solution 40.00 ml of an iodine solution (K = 0.9342 for 0.2N) were added. To titrate excess iodine 41.25 ml of a sodium thiosulphate solution (K = 0.9520 for 0.1N) were spent. Calculate the percentage of Na_2S in the sample.

48. A sample of anhydrous partly oxidized sodium sulphite weighing 2.2590 g is dissolved in a 200-ml volumetric flask. Calculate the percentage of Na_2SO_3 in the sample, if 20.00 ml of the solution are mixed with 40.00 ml of iodine solution, the amount of sodium thiosulphate spent for back titration is 23.16 ml, K_I = 1.1990 for 0.1N, and $K_{Na_2S_2O_3}$ = = 0.8822 for 0.1N.

49. If 10.00 ml of hydrogen sulphide water are mixed with 50.00 ml of an iodine solution and its excess is titrated with 32.79 ml of a sodium thiosulphate solution, calculate the percentage of H_2S in the water, when K_I is 1.1120 for 0.1N and $K_{Na_2S_2O_3}$ is 0.9730 for 0.1N.

50. A sample of sodium sulphite weighing 0.3878 g is dissolved and treated with 50.00 ml of an iodine solution, whose excess is titrated with 25.40 ml of a sodium thiosulphate solution. T_I is 0.01245; $T_{Na_2S_2O_3 \cdot 5H_2O}$ is 0.02502. Calculate the percentage of Na_2SO_3 in the sample.

Various Determinations by Oxidation-Reduction Methods

51. To determine the sulphur content of steel, sulphur is converted into H_2S by various methods. The hydrogen sulphide is oxidized with an iodine solution, whose excess is titrated with a sodium thiosulphate solution. Calculate the percentage of sulphur in a steel sample, given the following: mass of the sample, 3.0350 g; the amount of an iodine solution added, 10.80 ml; the amount of a sodium thiosulphate solution spent for titration, 5.65 ml; concentration of the iodine solution, 0.03523*N*; $K_{Na_2S_2O_3} = 1.0140$ for 0.05*N*.

52. The following data were obtained during the determination of sulphur in a steel sample: the mass of the sample, 3.1640 g; the amount of an iodine solution added, 5.00 ml; the amount of a sodium thiosulphate solution spent for titration, 3.34 ml; $K_I = 1.1740$ for 0.03*N*; the concentration of the sodium thiosulphate solution, 0.0507*N*. Calculate the percentage of sulphur in the sample.

53. A sample of steel weighing 10.0000 g was tested for sulphur (see Problem 51). The amount of an iodine solution added, 15.00 ml; the amount of sodium thiosulphate spent in titration, 8.50 ml; 1 ml of the iodine solution is equivalent to 0.98 ml of the sodium thiosulphate solution; $T_{I/S} = 0.0003079$. Calculate the percentage of sulphur in the sample.

54. The following data were obtained during the determination of sulphur in cast iron: the mass of the sample, 5.1620 g; the amount of an iodine solution added, 15.40 ml; the amount of a sodium thiosulphate solution spent in titration, 12.60 ml; 1 ml of the iodine solution is equivalent to 1.02 ml of the sodium thiosulphate solution; $T_{I/S} = 0.0006452$. Calculate the percentage of sulphur in the sample.

55. A sample of steel is tested for manganese. The sample, weighing 0.3510 g, is dissolved and manganese oxidized to permanganic acid. The amount of an Na_3AsO_3 solution ($K = 1.004$ for 0.03*N*) spent for the titration of $HMnO_4$ is 8.43 ml. Calculate the percentage of manganese in the sample.

56. A sample of steel weighing 0.3668 g was tested for manganese. The results of the determination are as follows:

the amount of a sodium arsenite solution spent for the titration of the permanganic acid produced during the analysis is 5.70 ml and the concentration of the sodium arsenite solution is 0.0315*N*. Calculate the percentage of manganese in the sample.

57. A sample of steel weighing 1.1584 g was tested for chromium, which was oxidized to chromic acid. To reduce the acid 16.00 ml of Mohr's salt solution were added. To titrate the excess Mohr's salt 2.70 ml of $KMnO_4$ solution were spent; 1.28 ml of the $KMnO_4$ solution are equivalent to 1.00 ml of Mohr's salt solution. Calculate the percentage of chromium in the sample if $T_{\text{Mohr's salt/Cr}} = 0.0008638$.

58. A sample weighing 1.017 g was tested for chromium. The sample was dissolved and oxidized. The chromic acid formed was reduced by 40.00 ml of Mohr's salt solution. To titrate the excess reductant 5.02 ml of potassium permanganate solution with a concentration of 0.02394*N* were used. If 10 ml of Mohr's salt are equivalent to 9.63 ml of $KMnO_4$ solution, calculate the percentage of chromium in the sample.

59. A sample of bronze weighing 0.9122 g was tested for tin as $SnSO_4$, which is usually titrated with a standard iodine solution in the absence of air. Calculate the percentage of tin in the bronze sample if 15.73 ml of iodine solution were spent for titration and the concentration of the iodine solution is 0.03523*N*.

60. A sample of brass weighing 1.0690 g is tested for tin (see Problem 59). The amount of iodine solution spent for titration is 2.90 ml, its concentration is 0.03666*N*. Calculate the percentage of tin in the sample.

61. A phenol sample weighing 1.1100 g was tested for purity by the bromide-bromate method. The sample was dissolved in a 500-ml volumetric flask, and 10.00 ml of the solution were treated with 50.00 ml of a bromide-bromate mixture ($K = 0.9870$ for 0.1*N*). To titrate the iodine which was liberated by the excess bromide-bromate mixture 35.20 ml of thiosulphate solution ($K = 1.0240$ for 0.1*N*) were used. Calculate the percentage of phenol in the preparation.

62. A sample of phenol weighing 0.5022 g is tested for purity. The capacity of the volumetric flask used for dissolving the sample is 250 ml; the amount of test solution is

10.00 ml; the amount of bromide-bromate mixture is 50.00 ml, and its K = 0.9867 for 0.1*N*; the amount of sodium thiosulphate solution spent for titration is 36.10 ml; its concentration is 0.1018*N*. Calculate the percentage of impurities in the sample.

Note: The determination of phenol (and other readily brominated organic substances) by the bromide-bromate method is based on the liberation of free bromine from the bromide-bromate mixture in an acid medium. The free bromine then reacts quantitatively as follows:

$$C_6H_5OH + 3Br_2 = C_6H_2Br_3OH + 3HBr$$
$$Br_2 + 2KI = I_2 + 2KBr$$

The phenol content of the original sample is determined by thiosulphate titration of the iodine liberated by the bromine which has not reacted with phenol. The calculations are the same as in other analyses by back titration.

63. A sample of potassium dichromate weighing 10.000 g is dissolved in a 2.00 litre volumetric flask in order to prepare a standard solution for chromatometric determinations. Determine the following: (a) the normality of the solution; (b) its titre against Fe_2O_3; (c) its titre against Sb.

64. A sample of pure $K_2Cr_2O_7$ weighing 1.2850 g is dissolved in a 500-ml volumetric flask. What amount, in ml, of this solution will be spent for the titration of 20.00 ml of a 0.0500*N* solution of Mohr's salt?

65. A sample of limestone weighing 1.2290 g was tested for Fe_2O_3. The liberated iron was passed into solution, reduced, and the solution diluted in a 250-ml volumetric flask with water to the mark. To titrate 25.00 ml of this solution 5.26 ml of potassium dichromate solution, whose T_{Fe} = 0.0003025, were used. Calculate the percentage of Fe_2O_3 in the sample.

66. A sample of a soldering alloy weighing 0.5442 g was appropriately treated, the recovered tin was reduced and titrated with 28.35 ml of a standard potassium dichromate solution (*K* = 0.9835 for 0.2*N*). Calculate the percentage of tin in the sample.

CHAPTER FIVE

NEUTRALIZATION METHODS

A. Theoretical principles

The main theoretical principles underlying the acid-base titration method are calculations and determinations of hydrogen ion concentration in solutions of various substances, such as acids, bases, salts, and mixtures of these substances formed in solutions during titration. For the sake of convenience, in calculations and graphic representations, two forms of expressing gram-ionic or molar concentrations of ions and substances are used, exponential and logarithmic. To express a quantity in the exponential form means to present it in the form of two cofactors, one of which is 10^n (where n can be both positive and negative quantities).

Example 1. Express 25.000, 1000, 0.001, and 0.00035 in the exponential form.

Solution. $25{,}000 = 2.5 \times 10^4$; $1000 = 1 \times 10^3$; $0.001 = 1 \times 10^{-3}$; $0.00035 = 3.5 \times 10^{-4}$ or 35×10^{-5}.

The above example shows that the exponent of 10 is equal to the number of figures through which the point separating the whole number from the fraction has been moved. If the point is moved to the left, the exponent is positive, and if to the right, negative. This method can be used to express not only concentrations of solutions but also any other quantities.

Concentrations and other values can conveniently be expressed logarithmically in most calculations associated with the neutralization methods of titration, in the form of the negative logarithms of the quantities. If we designate the negative logarithm by "p", then for a quantity a, the following holds true:

$$pa = -\log a$$

Example 2. Determine "p" for 0.00001.

Solution. $0.00001 = 10^{-5}$; $\log 10^{-5} = -5$; $-\log 10^{-5} = 5$; $p = 5$.

"p" *of any quantity expressed as a decimal fraction is equal to the number of decimal places of the fraction minus the logarithm of the quantity made by its significant figures.*

Example 3. Determine "p" of 0.00035.

Solution. The number of decimal places in the fraction is 5; $\log 35 = 1.54$; $p = 5 - 1.54 = 3.46$.

If we want to find a quantity by its known "p", the calculations are reversed.

Example 4. Find a quantity a if pa is 3.46.

Solution. From the definition of "p" it follows that if $pa = 3.46$, then $a = 10^{-3.46}$. But this is an inconvenient form of expression for calculations and the quantity should therefore be converted into decimal fraction by the following transformations:

$$a = 10^{-3.46} = 10^{(-4)+0.54} = 10^{-4} \times 10^{0.54} = 0.0001 \times$$

$$\times 3.5 = 0.00035.$$

If a number is $10^{0.54}$, the decimal logarithm is 0.54. The table of logarithms will show that the logarithm of 0.54 is 3.5.

Such calculations do not require particular accuracy (exceeding two significant figures), and the table of two-place logarithms given in the Appendix can therefore be used.

Determination of the following quantities used in the neutralization methods involve the calculation of "p": the hydrogen ion concentration (pH), the hydroxyl ion concentration (pOH), concentrations of acids, bases, and salts (pC_{acid}, pC_{base}, pC_{salt}); dissociation constants of acids, bases, and indicators (pK_{acid}, pK_{base}, pK_{ind}). All these calculations are done by the method illustrated in the examples above. When calculating pH and pOH, it is necessary to remember that $[H^+] = C_{acid}$ and $[OH^-] = C_{base}$ only for dilute solutions of strong acids and strong bases. In

all other cases values of pH and pOH should be calculated by special formulas given in courses of quantitative analysis.

*Problems**

1. What is the reaction of solutions of the following salts: potassium chloride, sodium bromide, zinc nitrate, copper sulphate?
2. What is the reaction of the following salt solutions: aluminium chloride, barium nitrate, sodium sulphate?
3. What is the reaction of solutions of the following salts: potassium carbonate, sodium sulphide, ferric sulphate?
4. What is the reaction of solutions of the following salts: silver nitrate, trisodium phosphate, ammonium chloride?
5. Acetic acid is titrated with potassium hydroxide solution to neutral reaction of the medium. Is the result correct? If not, then what is the sign of the error?
6. A solution of potassium hydroxide is titrated with acetic acid to neutral reaction. Is the result correct? If not, then what is the sign of the error?
7. Hydrochloric acid is titrated with ammonium hydroxide to neutral reaction of the medium. Is the result correct? If not, then what is the sign of the error?
8. Ammonium hydroxide is titrated with hydrochloric acid to neutral reaction of the medium. Is the result correct? If not, then what is the sign of the error?
9. Sulphuric acid is titrated with sodium hydroxide solution to a weakly acid reaction. Is the point of equivalence correctly determined? If not, then decide whether the solution is under- or overtitrated.
10. A solution of barium hydroxide is titrated with hydrochloric acid to a weakly acid reaction. Decide if the point of equivalence is determined correctly.
11. Express, in exponential form, the concentration of hydrogen ions in hydrochloric acid with the following normality (assuming $\alpha = 100\%$): 1; 0.1; 0.001; 0.000001.

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* Examples showing how to solve problems in this Section are given in the *Course of Analytical Chemistry* by A. P. Kreshkov and A. A. Yaroslavtsev, translated by MIR Publishers in 1977 (Part Two, Ch. 4).

12. Express, in exponential form, the concentration of hydroxyl ion in a solution of sodium hydroxide with the following molarity (assuming $\alpha = 100\%$): 0.01, 0.0001, 0.00001.

13. Express, in exponential form, the hydrogen ion concentration in hydrochloric acid with the following molarity (assuming $\alpha = 100\%$): 0.2, 0.0002, 0.05, 0.0005.

14. Express, in exponential form, the hydroxyl ion concentration in solutions of potassium hydroxide with the following molarity (assuming $\alpha = 100\%$): 0.03; 0.00003, 0.0035, 0.00052.

15. Determine the hydrogen ion concentration in $0.1N$ and $1M$ solutions of HNO_3, taking into account the degree of dissociation. Express the concentrations in exponential form.

16. Calculate the hydroxyl ion concentration in $0.1N$ and $1N$ solutions of KOH, taking into account the degree of dissociation. Express the concentrations in exponential form.

17. Determine the concentration of hydroxyl ion in $0.001M$ and $0.0001M$ solutions of HCl, assuming $\alpha = 100\%$.

18. Determine the hydrogen ion concentration in $0.01M$ and $0.00001M$ solutions of sodium hydroxide, assuming $\alpha = 100\%$.

19. The hydrogen ion concentration in a solution is 0.001 g-ion/litre. What is its pH?

20. The hydrogen ion concentration in a solution is 0.00001 g-ion/litre. Determine its pH.

21. The hydrogen ion concentration in a solution is 0.002 g-ion/litre. Determine its pH.

22. The hydrogen ion concentration in a solution is 0.0005 g-ion/litre. Determine its pH.

23. The hydroxyl ion concentration in a solution is 0.3 g-ion/litre. Determine the pH and pOH.

24. The hydroxyl ion concentration in a solution is 0.004 g-ion/litre. Determine the pOH and pH.

25. Determine the pH and pOH of a $0.006M$ solution of HCl (assuming $\alpha = 100\%$).

26. Determine the pH and pOH of $0.025M$ HCl (assuming $\alpha = 100\%$).

27. Determine the pH and pOH of $0.1M$ HCl, taking α into account.

28. Determine the pH and pOH of 1*M* HCl, taking α into account.

29. Determine the pOH and pH of 0.1*M* NaOH, taking α into account.

30. Determine the pOH and pH of 1*M* KOH, taking α into account.

31. A 0.1*N* solution of HCl is diluted with ten volumes of water. The solution obtained is diluted again with ten volumes of water. This procedure is performed seven times. How does the pH of the solution change after each new dilution? What is the pH of the solution after the sixth and the seventh dilution?

32. What is the approximate limits of the pH range?

33. To 20 ml of 0.1*N* HCl are added 30 ml of 0.1*N* NaOH. What is the pH of the resultant solution?

34. To 55 ml of 0.2*N* KOH are added 45 ml of 0.2*N* HCl. What is the pH of the resultant solution?

35. To 20 ml of 0.1*N* NaOH are added 10 ml of 0.15*N* HCl. Calculate the pH of the resultant solution.

36. To 500 ml of a 0.05*N* KOH solution are added 500 ml of a 0.04*N* HNO_3 solution. What is the pH of the resultant solution?

37. An equal volume of 0.15*N* NaOH is added to 0.2*N* HCl. Determine the pH and the pOH of the resultant solution.

38. To 1000 ml of a 0.001*N* HNO_3 solution is added 1 ml of a 1*N* KOH solution. Determine the pH and pOH of the resultant solution.

39. To 20 ml of a 0.04*N* HCl solution are added 45 ml of a 0.02*N* KOH solution. Determine the pH and pOH of the resultant solution.

40. To 15 ml of a 0.025*N* HCl solution are added 10 ml of a 0.050*N* NaOH solution. Determine the pH and pOH of the resultant solution.

41. The dissociation constant of CH_3COOH is $1.86 \times \times 10^{-5}$. Determine p*K*.

42. The dissociation constant of NH_4OH is 1.79×10^{-5}. Determine p*K*.

43. The concentration of CH_3COONa is 0.02*M*. Determine p*C*.

44. The concentration of NH_4Cl is 0.005*M*. Determine p*C*.

45. Determine $[H^+]$ of a solution if its pH is 2.6.
46. Determine $[H^+]$ of a solution if its pH is 5.2.
47. Determine $[H^+]$ of a solution if its pH is 8.
48. Determine $[H^+]$ of a solution if its pH is 9.4.
49. Determine $[H^+]$ of a solution if its pOH is 12.2.
50. Determine $[H^+]$ of a solution if its pOH is 13.5.
51. Determine $[OH^-]$ of a solution if its pH is 11.8.
52. Determine $[OH^-]$ of a solution if its pH is 10.3.
53. Determine the pH of a $0.1N$ CH_3COOH solution.
54. Determine the pOH of a $0.1N$ NH_4OH solution.
55. Determine the pH and $[H^+]$ of a $0.05N$ CH_3COOH solution.
56. Determine the pH and $[H^+]$ of a $0.002N$ HCOOH solution.
57. Determine the pH and $[H^+]$ of a $0.025N$ HNO_2 solution.
58. Determine the pH and $[H^+]$ of a $0.04N$ HCN solution.
59. Determine the pH and pOH of a $0.03N$ NH_4OH solution.
60. Determine the pH and pOH of a $0.5N$ NH_4OH solution.
61. Determine the pH of a $0.05N$ NH_4Cl solution.
62. Determine the pH of a $0.02N$ NH_4NO_3 solution.
63. Determine the pOH of a $0.2N$ NH_4Br solution.
64. Determine the pH of a $0.005N$ NH_4Cl solution.
65. Determine the pH of a solution at the point of equivalence during the titration of a $0.2N$ NH_4OH solution with hydrochloric acid of the same concentration.
66. Determine the pH of a solution at the point of equivalence during the titration of a $0.1N$ solution of NH_4OH with a $0.1N$ solution of hydrochloric acid.
67. At what pH should the titration of a $0.05N$ solution of NH_4OH with a $0.05N$ solution of H_2SO_4 be discontinued?
68. At what pH should the titration of a $0.2N$ solution of NH_4OH with a $0.1N$ solution of H_2SO_4 be discontinued?
69. Determine the pH of a $0.01N$ CH_3COOK solution.
70. Determine the pH of a $0.25N$ CH_3COONa solution.
71. Determine the pH of a $0.03N$ solution of HCOONa.
72. Determine the pH of a $0.04N$ solution of KCN.
73. Determine the pH of a solution at the point of equivalence during the titration of a $0.2N$ solution of CH_3COOH with a $0.2N$ solution of NaOH.

74. Determine the pH of a solution at the point of equivalence during the titration of a 0.1*N* solution of HCOOH with a 0.1*N* solution of KOH.

75. At what pH should the titration of a 0.1*N* solution of CH_3COOH with a 0.2*N* solution of NaOH be ended?

76. At what pH should the titration of a 0.1*N* solution of CH_3COOH with a 0.025*N* solution of KOH be ended?

77. If 250 ml of a 0.5*N* solution of NH_4OH contain 1.34 g of anhydrous NH_4Cl, what is the pH of the solution?

78. If 100 ml of a 0.2*N* solution of NH_4OH contain 1.07 g of anhydrous NH_4Cl, what is the pH of the solution?

79. If 5 ml of a 0.05*N* solution of HCl are added to 10 ml of a 0.05*N* solution of NH_4OH, determine the pH of the mixture.

80. If 15 ml of a 0.2*N* solution of HCl are added to 20 ml of a 0.2*N* solution of NH_4OH, determine the pH of the mixture.

81. If 10 ml of a 0.06*N* solution of H_2SO_4 are added to 10 ml of a 0.1*N* solution of NH_4OH, determine the pH of the mixture.

82. If 20 ml of a 0.2*N* solution of HNO_3 are added to 25 ml of a 0.3*N* solution of NH_4OH, determine the pH of the solution.

83. If 200 ml of a 0.1*N* solution of CH_3COOH contain 1.64 g of anhydrous sodium acetate, what is the pH of the solution?

84. If 500 ml of a 0.05*N* solution of HCOOH contain 1.7 g of anhydrous sodium formate, what is the pH of the solution?

85. Mix 50 ml of a 0.1*N* solution of CH_3COOH with 50 ml of a 0.1*N* solution of sodium acetate. What is the pH of the mixture?

86. Mix 100 ml of a 0.2*N* solution of HCOOH with 50 ml of a 0.5*N* solution of sodium formate. What is the pH of the mixture?

87. Mix 10 ml of a 0.2*N* solution of CH_3COOH with 5 ml of a 0.2*N* solution of NaOH. What is the pH of the mixture?

88. Mix 25 ml of a 0.05*N* solution of CH_3COOH with 20 ml of a 0.05*N* solution of KOH. What is the pH of the mixture?

89. Mix 15 ml of a 0.1*N* solution of HCOOH with 15 ml of a 0.05*N* solution of NaOH. What is the pH of the mixture?

90. Mix 20 ml of a 0.15*N* solution of CH_3COOH with 15 ml of a 0.12*N* solution of NaOH. What is the pH of the mixture?

91. Mix 10 ml of a 1*N* solution of NH_4OH with a drop of H_2SO_4 with a density of 1.84 g/cc. Determine the pH of the mixture.

92. Two drops of HCl with a density of 1.198 g/cc are added to 20 ml of a 0.1*N* solution of NH_4OH. Determine the pH of the mixture.

93. If 20.00 ml of a 0.2*N* solution of HCl are titrated with a 0.2*N* solution of NaOH determine the pH of the solution in the flask after the addition of the following quantities of alkali: (a) 10 ml; (b) 18 ml; (c) 20 ml.

94. If 20.00 ml of a 0.2*N* solution of NaOH are titrated with a 0.2*N* solution of HCl, determine the pH of the solution in the flask after the addition of the following quantities of the acid: (a) 10 ml; (b) 18 ml; (c) 20 ml.

95. If 25.00 ml of a 0.05*N* solution of HCl are titrated with a 0.05*N* solution of NaOH, calculate the points on the titration curve corresponding to the addition of 5, 12.5, 20.00, 22.50, 24.75, 24.98, 25, and 25.02 ml of the alkali.

96. If 25.00 ml of a 0.05*N* solution of KOH are titrated with a 0.05*N* solution of H_2SO_4, determine the points on the titration curve corresponding to the addition of 5, 12.5, 20.00, 22.50, 24.75, 24.98, 25.00, and 25.02 ml of the acid. Construct the graph.

97. If 20.00 ml of a 0.2*N* solution of CH_3COOH are titrated with a solution of KOH of the same concentration, determine the pH of the solution in the titration flask after the addition of the following quantities of the alkali: (a) 5, (b) 10, (c) 15, and (d) 20 ml.

98. If 25 ml of a 0.04*N* solution of HCOOH are titrated with a solution of NaOH of the same concentration, determine the pH of the solution in the titration flask after the addition of the following quantities of the alkali: (a) 2.5, (b) 12.5, (c) 19, and (d) 25 ml.

99. If 25 ml of a 0.2*N* solution of CH_3COOH are titrated with a solution of NaOH of the same concentration, calculate the points on the titration curve corresponding to the addition of 5, 10, 15, 20, 24, 24.5, 24.90, 24.95, and 25 ml of the alkali.

100. Construct the titration curve for the titration of 20 ml of a 0.2*N* solution of HCOOH with a KOH solution of the same concentration using the points calculated after the addition of 2, 6, 10, 18, 19.8, 19.98, 20 and 20.02 ml of the alkali.

101. If 20 ml of a 0.4*N* NH_4OH solution are titrated with a solution of H_2SO_4 of the same concentration, calculate the points on the titration curve corresponding to the addition of 2, 6, 10, 18, 20 ml of the acid.

102. Construct a titration curve for the titration of 25 ml of a 0.2*N* solution of NH_4OH with a solution of HCl of the same concentration, using the points corresponding to the addition of the following quantities of the acid: 2.5, 5, 10, 20, 22.5, 24.75, 24.98, 25, and 25.02 ml.

103. Calculate the pK_{ind} of neutral red.

104. Calculate the pK_{ind} of methyl red.

105. Determine the colour range of tropaeolin 00.

106. Determine the colour range of nitramine.

107. What will be the colour of pure water if phenolphthalein, methyl orange or litmus are added?

108. What shade will pure water be coloured on the addition of (a) tropaeolin 00, (b) neutral red, (c) nitramine?

109. What shade will phenolphthalein be coloured when added to 0.1*N* solutions of NH_4NO_3, Na_2SO_4, CH_3COONa?

110. What will be the colour of litmus, phenolphthalein, and methyl orange in a 0.2*N* solution of HCOONa?

111. If a solution is not coloured by phenolphthalein but is coloured red by litmus, what is the pH of the solution?

112. A solution is coloured red by litmus and yellow by methyl orange. What is the pH of the solution?

113. Mix equal volumes of a 0.2*N* solution of NH_4OH and HNO_3. What will the colour be of (a) methyl orange, (b) litmus, (c) phenolphthalein in the resultant solution?

114. If 10 ml of a 0.2*N* solution of NaOH are added to 20 ml of a 0.1*N* solution of CH_3COOH, what will the colour be of methyl red, litmus, and phenolphthalein in the obtained solution?

115. If 25 ml of a 0.2*N* solution of KOH are mixed with the same volume of H_2SO_4 of the same concentration, what will the colour be of (a) methyl red, (b) litmus, (c) phenolphthalein in the resultant solution?

116. Equal volumes of 0.1*N* solutions of NH_4OH and CH_3COOH are mixed. What will the colour be of (a) methyl orange, (b) litmus, (c) phenolphthalein in the resultant solution?

117. Which indicators change their colour at the point of equivalence during the titration of a 0.1*N* solution of HNO_3 and a 0.1*N* solution of CH_3COOH with a 0.1*N* KOH solution?

118. Which indicators locate the point of equivalence during the titration of a 0.2*N* solution of $Ba(OH)_2$ and a 0.2*N* solution of NH_4OH with a 0.2*N* solution of HCl?

119. Titrate a 0.2*N* solution of CH_3COOH with a 0.2*N* solution of KOH in the presence of methyl orange. Is the selection of the indicator correct? If not, where has the mistake been made?

120. Titrate a 0.05*N* solution of HCl with a KOH solution of the same concentration in the presence of phenolphthalein. Is the choice of the indicator correct? If not, give your reasons.

121. A 0.1*N* solution of HCOOH is titrated with NaOH solution of the same concentration in the presence of methyl red. Is the choice of the indicator correct? If not, what will the resulting error in titration be?

122. A 0.2*N* solution of NH_4OH is titrated with H_2SO_4 of the same concentration in the presence of phenolphthalein. Is the choice of the indicator correct? If not, give your reasons.

B. Preparing standard solutions

Problems

1. What quantity, in grams, of KOH is required to prepare 1.5 litres of an approximately 0.02*N* solution?
2. What quantity, in grams, of NaOH is required to prepare 0.5 litre of an approximately 0.2*N* solution?
3. What quantity, in ml, of KOH solution with a density of 1.291 g/cc is required to prepare 5 litres of an approximately 0.15*N* solution?
4. What quantity, in ml, of NaOH solution with a density of 1.53 g/cc is required to prepare 12 litres of an approximately 0.1*N* solution?

5. What quantity, in ml, of HCl with a density of 1.15 g/cc is required to prepare 1.5 litres of a 0.2*N* solution?

6. What quantity, in ml, of sulphuric acid with a density of 1.74 g/cc is required to prepare 2.5 litres of a 0.05*N* solution?

7. What quantity, in grams, of $Na_2B_4O_7 \cdot 10H_2O$ is required to prepare 500 ml of a solution for the standardization of an approximately 0.1*N* solution of HCl?

8. What quantity of anhydrous soda is required to prepare, in a 200-ml volumetric flask, a solution for the standardization of an approximately 0.05*N* solution of sulphuric acid?

9. What quantity, in grams, of a succinic acid should be taken to standardize an approximately 0.4*N* solution of NaOH by the method of separate samples, so that not more than 25 ml of the alkali solution is used for each titration?

10. What quantity, in grams, of crystalline oxalic acid should be taken to standardize an approximately 0.5*N* solution of KOH by the method of separate samples, so that about 25 ml of the alkali solution is used for each titration?

11. To standardize hydrochloric acid, a sample of anhydrous soda weighing 5.2060 g is dissolved in a 500-ml volumetric flask. The amount of the solution spent for the titration of 26.18 ml of HCl is 25 ml. Determine (a) the normality of the HCl solution, (b) K_{HCl}, (c) T_{HCl}, (d) $T_{HCl/NaOH}$.

12. To standardize sulphuric acid, a sample of pure $Na_2B_4O_7 \cdot 10H_2O$ weighing 2.4000 g is dissolved in a 200-ml volumetric flask. The amount of the prepared borax solution spent for the titration of 20 ml of the acid is 33.85 ml. Calculate the following: (a) the normality of the sulphuric acid; (b) $K_{H_2SO_4}$; (c) $T_{H_2SO_4}$; (d) $T_{H_2SO_4/Na_2O}$.

13. To standardize sulphuric acid, a sample of $Na_2C_2O_4$ weighing 1.6750 g is calcined in a platinum crucible to constant weight, transferred quantitatively into a 250-ml volumetric flask, and dissolved. The solution is diluted with water to the mark. The amount of the solution thus obtained used for the titration of 22.46 ml of the acid is 25.00 ml. Determine the following: (a) the normality of the sulphuric acid; (b) $K_{H_2SO_4}$; (c) $T_{H_2SO_4}$.

14. To standardize hydrochloric acid, 20.00 ml of sodium hydroxide solution with the titre 0.03982 are used. The

solution is diluted in a 200-ml volumetric flask with water to the mark. The amount of the HCl solution used for the titration of 20.00 ml of the solution obtained is 18.95 ml. Determine the following: (a) the normality of the acid; (b) K_{HCl}; (c) T_{HCl}.

15. To standardize a KOH solution, a sample of $H_2C_2O_4 \cdot 2H_2O$ weighing 5.9840 g is dissolved in a 1000-ml volumetric flask. The amount of the KOH solution spent for the titration of 25.00 ml of the solution obtained is 26.32 ml. Determine the following: (a) the normality of the KOH solution; (b) K_{KOH}; (c) $T_{KOH/HCl}$.

16. To standardize a solution of NaOH, a sample of succinic acid weighing 0.4826 g is dissolved in a 200-ml volumetric flask. The amount of the alkali solution spent for the titration of 20.00 ml of the solution obtained is 21.05 ml. Determine the following: (a) the normality of the alkali solution; (b) K_{NaOH}, (c) T_{NaOH/H_2SO_4}.

17. To titrate a solution containing 0.2584 g of anhydrous soda 21.35 ml of sulphuric acid are used. Determine the following: (a) $T_{H_2SO_4}$, (b) $T_{H_2SO_4/NaOH}$, (c) $K_{H_2SO_4}$.

18. To titrate a solution of 0.5120 g of pure $Na_2B_4O_7 \cdot 10H_2O$ we use 26.32 ml of HCl. Determine the following: (a) T_{HCl}, (b) T_{HCl/K_2O}, (c) the normality of HCl.

19. To standardize a solution of hydrochloric acid a sample of $Na_2C_2O_4$ weighing 0.1724 g was calcined to constant mass ($Na_2C_2O_4 = Na_2CO_3 + CO$) and dissolved in an arbitrary amount of water. The amount of the acid spent for titration is 27.65 ml. Calculate $T_{HCl/NaOH}$.

20. To standardize sulphuric acid 20.00 ml of NaOH ($T = 0.001920$) were titrated with 22.40 ml of H_2SO_4. Calculate $T_{H_2SO_4}$.

21. To standardize a KOH solution, 0.1495 g of succinic acid was dissolved in an arbitrary amount of water and the solution titrated with 25.15 ml of the KOH solution. Determine K_{KOH}.

22. A sample of $H_2C_2O_4 \cdot 2H_2O$ weighing 0.07920 g was dissolved and titrated with 24.12 ml of NaOH solution. Determine K_{NaOH}.

23. To titrate 20.00 ml of an HCl solution 18.68 ml of a 0.1*N* standard solution of NaOH are used. Determine the following: (a) K_{HCl}, (b) T_{HCl/Na_2O}.

24. To standardize a solution of sulphuric acid, 20.00 ml of a standard solution of borax with a concentration of 0.1*N* were prepared. If 19.20 ml of the H_2SO_4 solution were used for titration, determine (a) the normality of sulphuric acid, (b) $T_{H_2SO_4}$.

25. To standardize a KOH solution, 25.00 ml of it were titrated with 24.22 ml of a 0.1*N* standard solution of H_2SO_4. Determine the following: (a) K_{KOH}, (b) T_{KOH/SO_3}.

26. To standardize a NaOH solution, 18.05 ml of it were titrated with 15.00 ml of a 0.1*N* standard solution of HCl. Determine the following: (a) the normality of NaOH, (b) T_{NaOH}.

27. A 0.1*N* standard solution of sulphuric acid from an ampoule was diluted with water in a 500-ml volumetric flask to the mark. If 18.82 ml of a NaOH solution were used to titrate 20.00 ml of the H_2SO_4 solution, determine the following: (a) K_{NaOH}, (b) $T_{NaOH/HCl}$.

28. A 0.1*N* standard solution of NaOH from an ampoule was diluted with water in a 200-ml volumetric flask to the mark. If 25.68 ml of the solution were spent to titrate 25.00 ml of an HNO_3 solution, determine the following: (a) the normality of HNO_3, (b) $T_{HNO_3/NaOH}$.

29. Calculate the mass of a sample of caustic soda to be used for testing for Na_2O if it is dissolved in a 200-ml volumetric flask and titrated with an approximately 0.1*N* HCl solution.

30. Calculate the mass of a sample of soda ash for testing for purity if the capacity of the volumetric flask to be used is 200 ml and the concentration of the standard solution of sulphuric acid is about 0.1*N*.

31. Determine the mass of a sample of vitriol oil with a density of 1.75 g/cc, if it is to be used for testing for SO_3, if a 1000-ml flask is used, and if the concentration of the NaOH solution is about 0.05 *N*.

32. What quantity, in ml, of vitriol oil with a density of 1.75 g/cc should be taken for the determination of the monohydrate, if the capacity of the volumetric flask to be used is 500 ml and about 25 ml of an approximately 0.1*N* solution of KOH is needed for the titration of 25 ml of the prepared solution?

33. What quantity, in ml, of commercial hydrochloric acid with a density of 1.149 g/cc should be taken for the determination of HCl concentration, if 20 ml of a 0.2*N* NaOH solution are spent for the titration of 20 ml of the solution prepared by dissolving the acid sample in a 250-ml volumetric flask?

34. What quantity, in grams, of nitric acid with a density of 1.40 g/cc is required for a test for purity, if a 1000-ml volumetric flask and an approximately 0.04*N* KOH solution are used?

35. What quantity, in grams, of fuming sulphuric acid containing about 90 per cent of SO_3 should be taken for the determination of SO_3, if the capacity of the volumetric flask is 500 ml and the concentration of the KOH solution is about 0.5*N*?

36. What quantity, in grams, of oleum containing about 20 per cent of free SO_3 should be taken for the determination of total SO_3, if about 25 ml of an approximately 1*N* alkali solution are needed for the titration of 25 ml of a solution prepared by dissolving the sample in a 200-ml volumetric flask?

37. What quantity, in grams, of caustic soda should be taken for a test for NaOH, if about 30 ml of 0.5*N* HCl are to be used for the titration, in the presence of methyl orange, of the solution obtained by dissolving the sample?

38. What quantity, in grams, of soda ash should be taken for a test for purity, if about 30 ml of a 0.2*N* acid solution are to be used for the titration, in the presence of methyl orange, of a solution of the sample in an arbitrary amount of water?

39. What quantity, in grams, of KOH solution with a density of 1.41 g/cc should be taken for the determination of KOH if about 25 ml of an approximately 0.3*N* acid are to be spent for the titration of the solution obtained by dissolving the sample?

40. What quantity, in grams, of ammonia solution with a density of 0.91 g/cc should be weighed out, if about 35 ml of 1*N* sulphuric acid are to be spent for its titration?

41. What quantity, in grams, of an approximately 70 per cent nitric acid should be taken for a test for purity, if about 25 ml of a 1*N* alkali solution are to be used for the ti-

tration of the solution obtained by dissolving the sample?

42. What quantity, in grams, of oleum containing about 16 per cent of free SO_3 should be taken for the determination of SO_3 in the sample, if not less than 30 ml of a 1*N* alkali solution are to be used for the titration of the solution obtained by dissolving the sample?

C. Calculating the results of analyses

Problems

1. To titrate 20.00 ml of a NaOH solution 22.40 ml of HCl ($K = 0.9325$ for 0.1*N*) are used. What quantity, in grams of NaOH is contained in 1000 ml of the solution?

2. An unknown quantity of H_2SO_4 is dissolved in a 1000-ml volumetric flask. To titrate 25.00 ml of the solution 30.45 ml of a 0.1025*N* NaOH solution are used. What quantity, in grams, of H_2SO_4 has been dissolved in the flask?

3. A sample of caustic weighing 2.1060 g is dissolved in a 500-ml volumetric flask. The solution is used to titrate 25.00 ml of HCl solution ($K = 0.9850$ for 0.1*N*). The amount of alkali spent for titration is 24.50 ml. Calculate the percentage of Na_2O in the sample.

4. A sample of vitriol oil weighing 11.6500 g is dissolved in a 1000-ml volumetric flask. The solution is used to titrate 25.00 ml of KOH solution ($K = 1.1240$ for 0.2*N*). The amount of the solution spent for titration is 26.80 ml. Calculate the percentage of SO_3 in the sample.

5. A sample of potassium hydroxide weighing 7.6240 g is dissolved in a 500-ml volumetric flask. To titrate 25.00 ml of the solution 32.20 ml of HCl ($T_{HCl/Na_2O} = 0.006442$) are used. Calculate the percentage of KOH in the sample.

6. Using a burette 29.50 ml of sulphuric acid with a density of 1.553 g/cc are placed in a 1000-ml volumetric flask. To titrate 25.00 ml of a 0.5378*N* NaOH solution 22.20 ml of the resulting acid solution are used. Calculate the percentage of SO_3 in the sample.

7. A sample of soda ash weighing 0.1324 g is dissolved in an arbitrary amount of water and titrated, in the presence of

methyl orange, with 24.45 ml of hydrochloric acid (K = = 0.9850 for 0.1N). Calculate the percentage of Na_2CO_3 in the sample.

8. To neutralize a solution obtained by dissolving 0.1822 g of vitriol oil 30.30 ml of NaOH solution (T_{NaOH/H_2SO_4} = = 0.005020) are used. Calculate the percentage of SO_3 in the sample.

9. To titrate a solution obtained by dissolving 3.1580 g of potassium hydroxide 27.45 ml of hydrochloric acid solution ($T_{HCl/NaOH}$ = 0.07862) are used. Calculate the percentage of KOH in the sample.

10. To titrate a solution prepared by dissolving 2.3200 g of caustic soda 28.80 ml of a 1.9640N HCl are used. Calculate the percentage of Na_2O in the sample.

11. A titration flask contains distilled water. From a microburette 0.500 ml of vitriol oil with a density of 1.498 g/cc is added and the solution thus obtained is titrated with 41.94 ml of KOH (T_{KOH} = 0.01266). Calculate the percentage of H_2SO_4 in the sample.

12. To titrate a solution obtained by diluting 1.0000 ml of H_2SO_4 with a density of 1.716 g/cc 49.00 ml of NaOH solution (K = 1.1280 for 0.5N) are used. Calculate the percentage of SO_3 in the sample.

13. We dilute 50.00 ml of nitric acid, having a density of 1.40 g/cc, in a 1000-ml volumetric flask with water added to the mark. To titrate 20.00 ml of KOH solution (T_{KOH/H_2SO_4} = = 0.04904) 26.88 ml of the prepared acid solution are used. Determine the percentage of HNO_3 in the initial solution.

14. We place 25.00 ml of HCl with a density of 1.19 g/cc in a 500-ml volumetric flask and add water to the mark. To titrate 20.00 ml of the solution 25.13 ml of NaOH solution (T = 0.01976) are used. What is the normality of the initial acid solution and its per cent concentration?

15. To test oleum for SO_3 content a sample is placed in a weighed thin-wall glass ampoule. The ampoule is sealed and weighed again. It is then placed in a jar containing distilled water and crushed. The solution thus obtained is titrated with KOH solution. Determine the percentage of total, bound, and free SO_3 in the oleum, if the mass of the empty ampoule is 0.3580 g, the mass of the ampoule filled with oleum is 1.9790g, the concentration of the standard

alkali solution is 0.9980*N*, and the amount of alkali spent for titration is 35.53 ml.

16. Oleum is tested for SO_3 content as in the previous problem. The mass of the oleum sample is 2.1010 g, the concentration of the standard alkali (NaOH) solution is 1.1000*N*, and the amount of alkali spent for the titration of the dissolved sample is 40.67 ml. Calculate the percentage of total, bound, and free SO_3 in the sample.

17. A sample of crystalline soda weighing 7.2860 g is dissolved in a 250-ml volumetric flask. To titrate 25.00 ml of the solution, in the presence of methyl orange, 22.75 ml of sulphuric acid (T = 0.01020) are used. Calculate the percentage of Na_2CO_3 in the sample.

18. Sodium carbonate weighing 2.7350 g is dissolved in a 200-ml volumetric flask. To titrate 20.00 ml of the solution, in the presence of methyl orange, 18.65 ml of hydrochloric acid (T = 0.003854) are used. Calculate the percentage of water in the sample if it contains no appreciable quantities of extraneous impurities. Compare the result with the water content of an accurately decahydrous crystal hydrate.

19. A sample of freshly crystallized pure oxalic acid weighing 2.6910 g is dissolved in a 500-ml volumetric flask. To titrate 25.00 ml of a 0.09768*N* solution of sodium hydroxide 28.60 ml of the prepared solution are spent. Prove that the crystal hydrate of oxalic acid contains two molecules of water.

20. A sample of freshly crystallized pure sodium tetraborate weighing 1.6690 g is dissolved in a 200-ml volumetric flask. To titrate 20.00 ml of the solution 17.50 ml of sulphuric acid solution ($T_{H_2SO_4/KOH}$ = 0.002806) are used. Prove that the crystal hydrate contains ten molecules of water.

21. Equal volumes of KOH and H_2SO_4 solutions with (a) the same normality, (b) equal titres, and (c) equal corrections for normality are mixed. What is the reaction of each mixture?

22. Solutions of NaOH and HCl have the same titres ($T_{NaOH} = T_{HCl}$). In what proportion should the solutions be taken to neutralize each other?

23. To 25.00 ml of KOH solution of unknown concentration are added 50.00 ml of H_2SO_4 solution (*K* = 0.9500 for 0.1*N*). To titrate the excess acid 28.90 ml of NaOH solution

(K = 0.8570 for 0.1N) are spent. What is the normality of the KOH solution?

24. To 20.00 ml of HCl solution of unknown concentration are added 25.00 ml of KOH solution (K = 0.8000 for 0.1N). The resultant solution reacts strongly alkaline. The amount of H_2SO_4 solution (K = 1.200 for 0.1N) spent for back titration is 1.55 ml. Determine K_{HCl}.

25. While 25.00 ml of HNO_3 were being titrated with a 0.09562N KOH solution. The burette cock malfunctioned at the moment when the point of equivalence was approaching, and the solution was overtitrated. The amount of alkali added was 24.85 ml. To titrate excess alkali 0.58 ml of H_2SO_4 (K = 1.2450 for 0.05N) was spent. Determine the normality of HNO_3.

26. To 50.00 ml of HCl solution (K = 0.9500 for 0.2N) are added 25.00 ml of NaOH solution of unknown concentration. The resultant solution reacts acid. The amount of KOH (K = 1.2780 for 0.1N) spent for the final titration of the residual acid is 2.50 ml. Determine K_{NaOH}.

27. A sample of calcite weighing 1.5780 g was dissolved in 50.00 ml of hydrochloric acid (T = 0.04000). As soon as the sample had dissolved and the CO_2 removed from the solution, the solution was transferred to a 500-ml volumetric flask and water added to the mark. To titrate 50.00 ml of the resulting solution 23.45 ml of NaOH solution (T = 0.004000) were used. Calculate the percentage of $CaCO_3$ in the sample.

28. We place 3.6060 g of $Ba(OH)_2$ and 50 ml of HCl solution (K = 1.1200 for 0.5N) in a 200-ml volumetric flask. Water is added to the mark. The amount of this solution spent for the titration of 20.00 ml of KOH solution (T = = 0.0030) is 41.20 ml. Calculate the percentage of $Ba(OH)_2$ in the sample.

29. In testing ammonium chloride for purity by the Kjeldahl method ammonia is isolated from a sample weighing 0.5570 g and distilled into 100 ml of a 0.1968N solution of sulphuric acid. As soon as the distillation is complete, the solution is transferred into a 500-ml volumetric flask, and water added to the mark. The amount of alkali solution (K = 1.050 for 0.02N) spent for the titration of 25.00 ml of the resultant solution is 24.50 ml. Calculate the percentage of NH_4Cl in the sample.

30. The following data were obtained during the determination of ammonia in ammonium chloride: the mass of the sample, 0.7124 g; the concentration of the acid used for absorption of the liberated ammonia, 0.5120*N*; the volume of the acid spent for the reaction, 50.00 ml; the capacity of the volumetric flask containing the absorbing solution, 250 ml; the volume of the titrate, 25.00 ml; K_{KOH} = = 0.9740 for 0.05*N*; the amount of the solution spent for titration, 25.75 ml. Calculate the percentage of NH_3 in the sample.

31. The following data were obtained during analysis of amonium sulphate for nitrogen content: the mass of the sample, 1.8910 g; the volume of HCl solution taken for the absorption of NH_3, 200.00 ml; T_{HCl} = 0.008020; the capacity of the flask for dilution of the solution after the absorption of NH_3, 1000 ml; the volume of the titrate, 20.00 ml; the amount of NaOH solution spent for titration, 21.22 ml; T_{NaOH} = 0.0008000. Calculate the percentage of nitrogen in the sample.

32. A sample of flour weighing 7.0200 g was treated by the Kjeldahl method for the determination of nitrogen. Ammonia liberated from the sample was absorbed by 100.00 ml of sulphuric acid ($T_{H_2SO_4/KOH}$ = 0.02260). After the absorption of NH_3, the solution was transferred into a 200-ml volumetric flask and diluted with water to the mark. The amount of 0.1020*N* solution of KOH spent for the titration of 20.00 ml of the resultant solution was 19.61 ml. Calculate the nitrogen content of the flour.

33. A sample of zinc white weighing 2.000 g was dissolved in 100.00 ml of sulphuric acid (*K* = 0.9820 for 0.5*N*) for the determination of zinc oxide. The amount of alkali solution (*K* = 1.280 for 0.1*N*) spent for the titration of excess acid is 29.90 ml. Calculate the percentage of ZnO in the sample.

34. The ammonia obtained from 0.3967 g of an ammonium salt is added to 50.00 ml of HCl solution (*K* = 1.250 for 0.1*N*). The amount of NaOH solution (*K* = 0.980 for 0.1*N*) spent for the titration of excess HCl is 15.20 ml. Calculate the percentage of nitrogen in the salt.

35. Ammonia is distilled from 0.2229 g of an ammonium salt into 100.00 ml of HCl solution (*K* = 0.9658 for 0.1*N*). The amount of NaOH solution (*K* = 1.0720 for 0.1*N*) spent

for the titration of excess acid is 51.19 ml. Calculate the percentage of NH_3 in the salt.

36. The nitrogen contained in 0.8965 g of a fertilizer has been converted into ammonia, which is distilled into 100 ml of sulphuric acid solution (T = 0.009185). The amount of sodium hydroxide solution (K = 1.200 for 0.2N) spent for the titration of excess acid is 30.25 ml. Calculate the percentage of nitrogen in the sample.

37. A sample of calcite weighing 0.8679 g is dissolved in 25.00 ml of 0.7873N HCl, whose excess is titrated with 2.70 ml of 0.8818N NaOH solution. Calculate the percentage of $CaCO_3$ and CO_2 in the sample.

38. A sample of marble weighing 0.5668 g is dissolved in 30.00 ml of HCl (T = 0.02871). The amount of NaOH solution (0.8818N) spent for the titration of excess HCl is 14.10 ml. Calculate the percentage of non-carbonate impurities in the sample.

39. The following data are obtained from the analysis of synthetic ammonia water: the mass of an empty ampoule, 0.4252 g; the mass of the ampoule containing the sample, 1.6222 g; the volume of sulphuric acid solution taken for the absorption of NH_3, 40.00 ml; the concentration of the absorption solution, 1.004N; the volume of the NaOH solution spent for the titration of excess acid, 20.30 ml; the concentration of the alkali solution, 0.9650N. Calculate the percentage of NH_3 in the ammonia water.

40. A sample of nitric acid weighing 0.9654 g is placed, in an ampoule, in a jar containing water, to which 50.00 ml of 0.8919N NaOH solution has already been added. The ampoule is then crushed. The amount of HCl (T = 0.03550) spent for the titration of excess alkali is 35.20 ml. Calculate the percentage of HNO_3 and N_2O_5 in the sample.

41. A sample of sodium hydroxide weighing 0.9184 g was exposed to the air and part of it converted into soda by the action of atmospheric carbon dioxide. The sample was dissolved in a 250-ml volumetric flask, and 25.00 ml of the solution were titrated with 20.70 ml of 0.1042N HCl in the presence of phenolphthalein, and with 21.48 ml of the same acid in the presence of methyl orange. Calculate the percentage of NaOH and Na_2CO_3 in the sample.

42. A sample of sodium hydroxide weighing 0.2298 g was

partly converted into soda, dissolved in an arbitrary volume of water, and titrated with hydrochloric acid ($K = 0.897$ for $0.2N$). The amount of HCl spent for titration in the presence of phenolphthalein is 29.65 ml. Methyl orange is then added, and the titration is continued from the same burette without re-filling it with the acid. The titration is continued until the colour changes. The second reading of the burette is 30.90 ml. Calculate the percentage of NaOH and Na_2CO_3 in the sample.

43. A sample of soda weighing 0.1354 g and containing admixtures of sodium bicarbonate is dissolved in water and titrated with a $0.1028N$ solution of hydrochloric acid until the phenolphthalein colour vanishes. The reading of the burette at this moment is 10.25 ml. Without re-filling the burette the titration is continued with methyl orange. The second reading is 23.24 ml. Calculate the percentage of Na_2CO_3 and $NaHCO_3$ in the sample.

44. A sample of soda weighing 1.0140 g and containing admixtures of sodium bicarbonate is dissolved in a 200-ml volumetric flask. Firstly, 20.00 ml of the solution are titrated with 8.72 ml of H_2SO_4 ($T = 0.004920$) in the presence of phenolphthalein. The titration is then continued in the presence of methyl orange with the same acid from the same burette without re-filling it. The second reading is 18.10 ml. Calculate the percentage of Na_2CO_3 and $NaHCO_3$ in the sample.

45. A sample containing Na^+ and CO_3^{2-} ions and weighing 0.3106 g is dissolved in water. The solution reacts alkaline. The amount of sulphuric acid ($T = 0.0120$) spent for titration in the presence of phenolphthalein is 26.20 ml and in the presence of methyl orange, 29.30 ml. Calculate the percentage composition of the sample.

46. A sample of a substance containing the ions K^+ and CO_3^{2-} and weighing 0.3667 g is dissolved in water. The solution reacts alkaline. The amount of hydrochloric acid ($K = 1.1150$ for $0.2N$) spent for the titration of the solution in the presence of phenolphthalein is 21.15 ml and in the presence of methyl orange, 22.50 ml. Calculate the percentage of the main components of the substance in the sample.

47. The amount of HCl ($K = 0.9560$ for $0.2N$) spent for the titration of an alkaline solution is 7.52 ml in the pres-

ence of phenolphthalein and 18.25 ml in the presence of methyl orange. What components are contained in the solution and in what quantities if the ion K^+ is the only cation and the ion CO_3^{2-} is the only anion?

48. A sample of a substance containing the ions K^+ and CO_3^{2-} and weighing 0.2800 g is dissolved in water. The solution reacts alkaline. The amount of HCl ($K = 1.5210$ for $0.1N$) spent for the titration of the solution in the presence of phenolphthalein is 5.14 ml and in the presence of methyl orange, 21.45 ml. Calculate the percentage of the main components in the sample.

49. A sample of a substance (carbonate) containing the only cation Na^+ and weighing 0.5164 g is dissolved in water. As the solution is titrated with HCl ($K = 1.020$ for $0.2N$) in the presence of phenolphthalein, the latter is immediately decolourized, while the amount of acid for the titration of the solution in the presence of methyl orange is 29.30 ml. Identify the substance. Calculate the percentage of the main component in the sample.

50. A sample of an unknown substance containing only ions of potassium and carbonic acid residue and weighing 0.3810 g is dissolved in water. The solution reacts slightly alkaline. When the solution is titrated with HCl ($T = 0.003780$) in the presence of phenolphthalein the solution is decolourized by the first drops of the acid, while the amount of the acid spent for the titration of the solution in the presence of methyl orange is 32.40 ml. What is the main component of the sample? What is the percentage?

51. The amount of $0.5100N$ sulphuric acid spent for the titration of a solution of 0.7092 g of a sodium alkaline substance is 12.95 ml in the presence of phenolphthalein and 26.02 ml in the presence of methyl orange. What is the percentage of the main component in the sample?

52. A sample of an alkaline potassium substance weighing 0.2590 g is dissolved in water and titrated with sulphuric acid ($T = 0.005142$). The amount of acid spent for titration in the presence of phenolphthalein is 14.86 ml and in the presence of methyl orange, 29.70 ml. What is the main component of the sample? What is its percentage?

53. A mixture of sulphuric and phosphoric acids measuring 5.00 ml is placed in a 250-ml volumetric flask and water

added to the mark. The amount of a 0.08264*N* solution of NaOH spent for the titration of 25.00 ml of the solution in the presence of methyl orange is 30.15 ml. During this process all the sulphuric acid is neutralized, while phosphoric acid is titrated to a monosubstituted salt:

$$H_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O$$
$$H_3PO_4 + NaOH = NaH_2PO_4 + H_2O$$

When the solution is finally titrated in the presence of phenolphthalein (without re-filling the burette), the overall amount of NaOH spent for titration is 44.90 ml. During the second stage of the titration the monosubstituted salt is converted into the disubstituted one:

$$NaH_2PO_4 + NaOH = Na_2HPO_4 + H_2O$$

What quantity, in grams, of each acid is contained in 1000 ml of the mixture?

54. A mixture of sulphuric and phosphoric acids is analysed to determine the content of each acid in the mixture. The data of the analysis are as follows: the volume of the mixture, 10.00 ml; the capacity of a volumetric flask for dilution of the sample, 500 ml; the volume of the titrate, 20.00 ml; $T_{NaOH} = 0.003986$; the amount of NaOH solution spent for the titration of the mixture in the presence of phenolphthalein, 29.80 ml, and in the presence of methyl orange, 18.45 ml. (For more details see Problem 53.) What quantities, in grams, of sulphuric and phosphoric acids are contained in 1000 ml of the mixture?

55. To prepare phosphoric acid from phosphorite excess sulphuric acid is required, because $Ca(H_2PO_4)_2$ is formed when it is in deficit. The process is controlled by determining H_2SO_4, H_3PO_4, and $Ca(H_2PO_4)_2$ in the reaction mixture. Analysis of the reaction mixture gives the following results: the volume of the sample, 5.00 ml; the capacity of a volumetric flask for dilution of the sample, 200 ml; the titrate volume, 20.00 ml; the concentration of the standard solution of KOH, 0.1000*N*; the amount of the alkali spent for titration with methyl orange, 10.00 ml, and with phenolphthalein, 21.40 ml. What components are contained in the mixture: H_2SO_4 and H_3PO_4 or H_3PO_4 and $Ca(H_2PO_4)_2$? What quantity, in grams, of each

component is contained in 1000 ml of the solution, if reactions similar to those specified in Problem 53 occur during analysis?

56. The same liquid as in Problem 55 is subjected to analysis. The volume of the sample is 5.00 ml; the capacity of the volumetric flask for dilution is 250 ml; the volume of the titrate, 25.00 ml; $K_{KOH} = 0.9789$ for $0.1N$; the amount of the titrant spent for titration with phenolphthalein, 34.60 ml, and with methyl orange, 21.40 ml. What components are contained in the mixture: H_3PO_4 and H_2SO_4 or H_3PO_4 and $Ca(H_2PO_4)_2$? What quantity, in grams, of each component is contained in 1000 ml of the test solution?

57. The carbonate hardness of water is determined by the following chemical reactions:

$$Ca(HCO_3)_2 + 2HCl = CaCl_2 + 2CO_2 + 2H_2O$$

$$Mg(HCO_3)_2 + 2HCl = MgCl_2 + 2CO_2 + 2H_2O$$

The volume of a water sample taken for testing for hardness is 100.00 ml, while the amount of a $0.1103N$ solution of hydrochloric acid spent for the titration of the water is 2.44 ml. Express the hardness (a) in mg-equiv/litre and (b) in German degrees of hardness (1° = 1 mg CaO in 100 ml of water).

58. The amount of HCl (T = 0.004023) spent for the titration of 200.00 ml of water is 2.60 ml. Determine the carbonate hardness of water (a) in mg-equiv/litre and (b) in German degrees of hardness (see Problem 57).

59. The volume of a water sample taken for testing for removable (carbonate) hardness is 200.00 ml and the amount of HCl (T = 0.004102) spent for titration is 3.84 ml. Determine the hardness of the water and express it (a) in mg-equiv/litre, and (b) in French degress (1° = 1 mg of $CaCO_3$ in 100 ml).

60. Analyse water for hardness, when the volume of the sample is 100.00 ml; $K_{HCl} = 0.9968$ for $0.1N$; the amount of HCl spent for titration is 1.20 ml. Determine the removable (carbonate) hardness of the sample (a) in mg-equiv/litre; (b) in English degrees of hardness (1° = = 1 mg of $CaCO_3$ in 70 ml).

61. Determine the total hardness of industrial water. In order to convert the removable hardness into permanent hardness a 100.00-ml sample of water is treated with 25.00 ml of an alkali mixture ($Na_2CO_3 + NaOH$) whose total normality is 0.0965. The solution and the precipitate ($CaCO_3$ and $Mg(OH)_2$) are transferred quantitatively into a 200-ml volumetric flask and water is added to the mark. The amount of a 0.1020*N* solution of HCl spent for the titration of excess alkali in 100 ml of the filtrate is 5.85 ml. Determine the total hardness of the water (a) in mg-equiv/litre, and (b) in German degrees of hardness (see Problem 57).

62. Analyse a sample of water for hardness. The volume of the water sample is 100 ml; the amount of HCl spent for the titration of the removable hardness and its conversion into permanent hardness is 1.08 ml; the volume of the alkali mixture required to precipitate the ions Ca^{2+} and Mg^{2+} is 25.00 ml; the capacity of the volumetric flask into which the solution and the precipitate are transferred is 250 ml; the volume of the filtrate taken for the titration of excess alkali is 100.00 ml; the amount of HCl spent for the titration of excess alkali is 5.13 ml; $K_{HCl} = 1.103$ for 0.1*N*; $K_{alk.\ mix.} = 0.7625$ for 0.1*N*. Determine (a) the removable (carbonate) hardness; (b) total hardness, and (c) permanent (non-carbonate) hardness of the water, expressing it in German degrees of hardness (see Problem 57).

63. If 200 ml of water contain 4.28 mg of the ion Ca^{2+} and 2.13 mg of the ion Mg^{2+}, determine the total hardness of the water, expressing it (a) in mg-equiv/litre, (b) in German degrees of hardness, (c) in French, and (d) in English degrees of hardness (see Problems 57-60).

64. Water is saturated with magnesium carbonate. Determine its hardness, expressing it (a) in mg-equiv/litre, (b) in German, (c) in French, and (d) in English degrees of hardness.

65. The production of soda by the ammonia method is controlled by analysing the reaction mixture in order to determine free ammonia [in NH_4OH and $(NH_4)_2CO_3$], bound ammonia (in salts of other acids), and total ammonia. Free ammonia is determined by direct titration with an

acid, by which reaction it is converted into bound ammonia. Total ammonia is determined from ammonia salts by the formaldehyde method:

$$4NH_4Cl + 6HCHO = (CH_2)_6N_4 + 4HCl + 6H_2O$$

The acid which is liberated in this reaction is equivalent quantitatively to the reacted ammonia and is titrated with alkali. The following data are obtained during the determination of NH_3 by this method: the volume of the sample, 10.00 ml; the amount of acid spent for titration, 12.15 ml; the concentration of the acid, 0.9659*N*; the amount of alkali spent for the titration of the acid formed in the reaction, 45.60 ml; the concentration of the alkali solution, 0.9890*N*. Determine the quantity, in grams, contained in 1000 ml of the sample, of (a) free ammonia, (b) total ammonia, (c) bound ammonia.

66. The volume of the reaction mixture taken for the determination of ammonia is 15.00 ml. The amount of HCl (T = 0.03672) spent for the titration of the ammonia is 14.80 ml. The amount of a 1.012*N* solution of alkali spent for the titration of the acid formed during the formaldehyde treatment of the titrated solution is 48.50 ml. Determine the mass of bound ammonia in 1000 ml of the reaction mixture.

CHAPTER SIX

PRECIPITATION AND COMPLEXATION

A. Preliminary Calculations and Calculations Involving the Standardization of Solutions

Problems

1. What quantity, in grams, of silver nitrate is required to prepare 250 ml of an approximately 0.05*N* solution?
2. What quantity, in grams, of silver nitrate is required to prepare 1.5 litres of an 0.1*N* solution?
3. What quantity, in grams, of pure silver is required to prepare 200 ml of a solution for the standardization of an approximately 0.1*N* solution of NH_4SCN?
4. What quantity, in grams, of silver containing 3.98 per cent of impurities should be taken to prepare 250 ml of a precisely 0.025*N* solution?
5. What quantity, in grams, of pure KCl should be taken to prepare a solution for the standardization of an approximately 0.1*N* solution of $AgNO_3$ using a 500-ml volumetric flask?
6. Calculate the mass of pure NaCl required to prepare 250 ml of an approximately 0.05*N* solution to be used for the standardization of a silver nitrate solution.
7. Calculate the mass of pure NaCl which should be used to standardize an approximately 0.1*N* solution of $AgNO_3$ by the method of separate samples, using a 50-ml burette.
8. What quantity, in grams, of pure NaCl should be taken to standardize an approximately 0.05*N* solution of $AgNO_3$ so that no more than 25 ml of the salt solution will be used for titration?
9. What quantity, in grams, of ammonium thiocyanate should be taken to prepare 0.5 litre of an approximately 0.1*N* solution?
10. What quantity, in grams, of ammonium thiocyanate should be taken to prepare 750 ml of an approximately 0.05*N* solution?

11. A sample of pure KCl weighing 1.4960 g is dissolved in a 200-ml volumetric flask. What quantity, in ml, of 0.100*N* $AgNO_3$ is required to standardize 20.00 ml of the KCl solution?

12. A sample of pure NaCl weighing 0.8142 g is dissolved in water to prepare 250 ml of solution. What quantity, in ml, of a 0.0500*N* solution of $AgNO_3$ is required to standardize 25 ml of the NaCl solution?

13. What quantity, in ml, of a 0.05*N* solution of $AgNO_3$ is required to standardize 20.00 ml of a solution obtained by dissolving 0.1052 g of pure NaCl in water?

14. Decide whether it is possible to use a sample of pure KCl weighing 0.3782 g to standardize a 0.1*N* solution of $AgNO_3$ by the method of separate samples using a 50-ml burette.

15. What quantity, in ml, of $AgNO_3$ solution (T = = 0.01760) will be used to titrate 25.00 ml of a solution obtained by dissolving 1.1820 g of pure NaCl in a 250-ml volumetric flask?

16. What quantity, in ml, of $AgNO_3$ solution ($T_{AgNO_3/Ag}$ = = 0.005040) will be spent to titrate 20.00 ml of a solution obtained by dissolving 0.1000 g of pure KCl in a 250-ml volumetric flask?

17. What quantity, in ml, of $AgNO_3$ solution ($T_{AgNO_3/Ag}$ = = 0.005000) will be spent to titrate 25.00 ml of NaCl solution (T = 0.005000)? Both titres are expressed by the same number.

18. Potassium chromate and 30.00 ml of $AgNO_3$ solution (*K* = 1.060 for 0.1*N*) are added to a solution obtained by dissolving 0.2130 g of KCl. What is the colour of the contents of the flask?

19. KCl and NaCl solutions have the same titres. The titration of which requires more $AgNO_3$ solution if their initial volumes are the same? By how many times?

20. KCl and $AgNO_3$ solutions have the same titres. How do their volumes relate at the point of equivalence?

21. Calculate the mass of a sample of table salt containing about 80 per cent of NaCl which is required for testing for chlorine. The capacity of the volumetric flask is 500 ml and the concentration of $AgNO_3$ solution is 0.05*N*.

22. Calculate the mass of a sample of ammonium chloride containing about 50 per cent of chlorine for testing for chlorine, if the capacity of the volumetric flask is 250 ml and the concentration of $AgNO_3$ solution is about $0.1N$.

23. Determine the mass of a sample of sodium nitrate containing about 1.5 per cent of chlorine if it is to be used for testing for chlorine (see Problem 21).

24. Calculate the mass of a sample of barium chloride containing about 30 per cent of chlorine which is to be used for testing for chlorine (see Problem 22).

25. Calculate the mass of a sample of carnallite containing about 40 per cent of chlorine to be used for testing for chlorine by the method of separate samples using a $0.1N$ solution of $AgNO_3$ and a 50-ml burette.

26. What quantity, in grams, of sal ammoniac containing about 60 per cent of chlorine should be taken for analysis if the amount of a $0.05N$ $AgNO_3$ solution intended to be used for titration is 25 ml?

27. What quantity, in grams, of table salt containing about 15 per cent of moisture should be taken so that $AgNO_3$ solution ($T = 0.01425$) about half-filling a burette of 25-ml capacity will be used for the titration of the salt solution?

28. Calculate the mass of a sample of carnallite containing about 10 per cent of free moisture if it is to be used for determining chlorine by the method of separate samples. The concentration of $AgNO_3$ solution is $0.2N$ and the capacity of the burette is 25 ml.

29. A sample of pure sodium chloride is dissolved in a 500-ml volumetric flask. To 25 ml of the solution are added 50 ml of a $0.1N$ solution of $AgNO_3$. The amount of a $0.1N$ solution of NH_4SCN spent for the titration of excess $AgNO_3$ is 25 ml. Determine the mass of the sample.

30. A sample of pure ammonium chloride is dissolved in a 200-ml volumetric flask. To 20 ml of the obtained solution 40 ml of a $0.05N$ $AgNO_3$ solution are added. The amount of a $0.1N$ solution of NH_4SCN spent for the titration of excess $AgNO_3$ is 12.50 ml. Determine the mass of the sample.

31. A sample of pure potassium chloride weighing 0.9330 g is dissolved in a 250-ml volumetric flask. What quantity, in ml, of $0.1N$ $AgNO_3$ should be taken to precipitate

chlorine from 25.00 ml of the obtained solution, so that 25.00 ml of a 0.05*N* solution of NH_4SCN will be used to titrate excess silver?

32. A sample of pure sodium chloride weighing 3.00 g is dissolved in a 500-ml volumetric flask. What quantity, in ml, of a 0.100*N* solution of $AgNO_3$ should be spent to treat 20.00 ml of the solution so that 25.00 ml of a 0.0500*N* solution of NH_4SCN will be used for the titration of excess silver?

33. A sample of pure ammonium chloride containing 15 per cent of free moisture is dissolved in water. If 50.00 ml of $AgNO_3$ solution (T = 0.0338) are added to the solution and 25.00 ml of a 0.05*N* solution of NH_4SCN are used for the titration of excess $AgNO_3$, calculate the mass of the sample.

34. Calculate the mass of a sample of carnallite used for determining chlorine, if the amount of NH_4SCN solution (T = 0.003808) to be spent for the titration of excess silver after the dissolving of the sample and its precipitation with 20.00 ml of a 0.1*N* solution of $AgNO_3$ is to be 25.00 ml.

35. What quantity, in grams, of an alloy containing 84 per cent of silver should be dissolved in nitric acid, so that after dilution of the obtained solution with water in a 200-ml volumetric flask 25.00 ml of a 0.1*N* solution of NH_4SCN will be spent to titrate the same volume of the solution?

36. What quantity, in grams, of pure silver should be dissolved in nitric acid with subsequent dilution with water in a 100-ml volumetric flask, if 20.00 ml of NH_4SCN solution (T = 0.00400) are to be spent to titrate the same quantity of the obtained solution?

37. What quantity, in grams, of an alloy containing 90 per cent of Ag should be dissolved so that not less than 25 and not more than 50 ml of a 0.1*N* solution of NH_4SCN will be spent to titrate the obtained solution?

38. Determine the limits of the mass of a sample of pure Ag so that after it is dissolved in nitric acid and diluted with water not less than 12 and not more than 25 ml of ammonium thiocyanate (T = 0.0080) will be spent to titrate the obtained solution.

39. Calculate the titre of NH_4SCN solution so that 25.00 ml of it will titrate the same volume of a solution obtained by dissolving 2.6970 g of pure silver in nitric acid with subsequent dilution with water in a 250-ml flask.

40. Find the normality of a solution of ammonium thiocyanate so that 20.00 ml of it will titrate a solution obtained by dissolving 0.2100 g of an alloy containing 84 per cent of silver.

41. A sample of pure sodium chloride weighing 2.9010 g is dissolved in a 1000-ml volumetric flask. For 25.00 ml of this solution 25.80 ml of an $AgNO_3$ solution being standardized are used. Determine the following: (a) the normality of the $AgNO_3$ solution; (b) K_{AgNO_3}; and (c) titre of the $AgNO_3$ solution.

42. A sample of pure potassium chloride weighing 3.8460 g is dissolved in a 500-ml volumetric flask. To titrate 20.00 ml of this solution 18.40 ml of a silver solution being standardized are used. Determine the following: (a) the normality of the $AgNO_3$ solution; (b) K_{AgNO_3}; and (c) $T_{AgNO_3/Ag}$.

43. The amount of an $AgNO_3$ solution used for the titration of a solution prepared by dissolving 0.1020 g of NaCl is 38.40 ml. Determine the following: (a) the normality of the $AgNO_3$ solution; (b) K_{AgNO_3}; and (c) $T_{AgNO_3/Cl}$.

44. A sample of pure potassium chloride weighing 0.1560 g is dissolved and titrated with 41.20 ml of $AgNO_3$ solution. Determine the following: (a) the normality of the $AgNO_3$ solution; (b) K_{AgNO_3}; (c) $T_{AgNO_3/Br}$.

45. The amount of an $AgNO_3$ solution spent for the titration of 25.00 ml of sodium chloride solution ($T_{NaCl/Cl} = 0.001890$) is 24.30 ml. Determine the following: (a) the normality of the $AgNO_3$ solution; (b) K_{AgNO_3}; and (c) T_{AgNO_3/NH_4SCN}.

46. If 21.12 ml of $AgNO_3$ are used for the titration of a solution obtained by dissolving 0.1204 g of NaCl, determine the following: (a) $T_{AgNO_3/I}$; (b) the normality of the $AgNO_3$ solution; and (c) K_{AgNO_3}.

47. A sample of pure sodium chloride weighing 0.1740 g is dissolved and titrated with 30.22 ml of an $AgNO_3$ solution. If 19.85 ml of an NH_4SCN solution are spent for the titration of 20.00 ml of the $AgNO_3$ solution, determine the fol-

lowing: (a) the normality of the NH_4SCN solution; (b) $T_{NH_4SCN/Ag}$.

48. A sample of potassium chloride weighing 0.1220 g is dissolved and titrated with 35.40 ml of an $AgNO_3$ solution, 25.00 ml of which can be titrated with 26.60 ml of an NH_4SCN solution. Determine T_{NH_4SCN}.

49. A sample of pure sodium chloride weighing 0.1810 g is dissolved and titrated with 30.65 ml of an $AgNO_3$ solution, 25.00 ml of which can be titrated with 24.20 ml of NH_4SCN. Determine the titre and normality of the ammonium thiocyanide solution.

50. A sample of pure potassium chloride weighing 0.3142 g is dissolved and titrated with 38.75 ml of an $AgNO_3$ solution, 20.00 ml of which are equivalent to 18.80 ml of an ammonium thiocyanide solution. Determine the normality and the titre of the ammonium thiocyanide.

B. Calculations in analyses with direct and back titration

Problems

1. A sample of a chloride weighing 1.4265 g is dissolved in a 250-ml volumetric flask and tested for chlorine content. If 19.95 ml of a 0.1055*N* $AgNO_3$ solution are spent for the titration of 20.00 ml of the solution, calculate the percentage of chlorine in the sample.

2. A sample of a mixture of sodium chloride and sodium nitrate weighing 0.8180 g is dissolved in a 200-ml volumetric flask. If 18.35 ml of an $AgNO_3$ solution ($T_{AgNO_3/KCl}$ = = 0.003442) are spent for the titration of 20.00 ml of the solution, calculate the percentage of NaCl in the sample.

3. A sample of sodium chloride weighing 2.4080 g is dissolved in a 500-ml volumetric flask. If 20.35 ml of an $AgNO_3$ solution (K = 0.9860 for 0.1*N*) are spent for the titration of 25.00 ml of the solution, calculate the percentage of chlorine in the sample.

4. A sample of $BaCl_2 \cdot 2H_2O$ weighing 6.7000 g is dissolved in a 1000-ml volumetric flask. If 28.95 ml of an $AgNO_3$ solution ($T_{AgNO_3/Ag}$ = 0.005120) are spent for the

titration of 25.00 ml of the solution, calculate the percentage of chlorine in the sample.

5. A sample of brine measuring 10.00 ml is diluted in a 500-ml volumetric flask. If 24.42 ml of an $AgNO_3$ solution ($K = 0.9245$ for $0.1N$) are spent for the titration of 25.00 ml of the solution, what quantity, in grams, of NaCl does one litre of the brine contain?

6. What quantity, in grams, of HCl is contained in 1000 ml of hydrochloric acid if 25.00 ml of it are neutralized and diluted with water in a 250-ml volumetric flask and the amount of a $0.9850N$ solution of $AgNO_3$ spent for the titration of 20.00 ml of the solution is 24.37 ml?

7. A sample of a silver alloy weighing 1.7450 g is dissolved in nitric acid. The solution is diluted with water in a 200-ml volumetric flask. The amount of ammonium thiocyanide ($K = 0.9344$ for $0.05N$) spent for the titration of 10.00 ml of the obtained solution is 11.75 ml. Calculate the percentage of silver in the alloy.

8. A sample of a silver salt weighing 1.5150 g is dissolved to give 250 ml of solution. The amount of ammonium thiocyanide ($T_{NH_4SCN} = 0.003568$) spent for the titration of 15.00 ml of the solution is 11.25 ml. Calculate the percentage of $AgNO_3$ in the sample.

9. If 28.60 ml of $AgNO_3$ ($K = 0.9120$ for $0.05N$) are spent for the titration of a solution prepared by dissolving 0.0973 g of a chloride in water, calculate the percentage of chlorine in the sample.

10. A sample of potassium bromide weighing 0.3038 g is dissolved in water and tested for purity. The solution is titrated with 23.80 ml of $AgNO_3$ ($T_{AgNO_3/Cl} = 0.003546$). Calculate the percentage of KBr in the sample.

11. A silver alloy weighing 0.2122 g is dissolved and titrated with 32.40 ml of ammonium thiocyanide ($K = 1.0200$ for $0.05N$). Calculate the percentage of silver in the alloy.

12. A sample of a silver alloy weighing 0.1900 g is dissolved. The amount of a $0.0500N$ NH_4SCN solution spent for the titration of the solution is 21.12 ml. Calculate the silver content of the alloy.

13. A sample of zinc ore weighing 3.1540 g is dissolved and diluted in a 250-ml volumetric flask. The amount of

potassium ferrocyanide ($T_{K_4Fe(CN)_6/ZnO} = 0.01285$) spent for the titration of 20.00 ml of the obtained solution is 4.90 ml. Calculate the zinc content of the sample.

14. A sample of a zinc salt weighing 0.2775 g is tested for zinc content. The amount of potassium ferrocyanide ($T_{K_4Fe(CN)_6} = 0.03876$) spent for the titration of the sample solution is 6.48 ml. Calculate the zinc content of the sample, calculating for ZnO.

15. A sample of a chloride weighing 1.4790 g is dissolved in a 250-ml volumetric flask and 25.00 ml of the solution are treated with 50.00 ml of $AgNO_3$ ($K = 0.9580$ for $0.1N$). The amount of ammonium thiocyanide ($K = 1.1200$ for $0.1N$) spent for the titration of excess silver is 25.50 ml. Calculate the percentage of chlorine in the chloride. What cation does the chloride molecule contain?

16. A sample of potassium chloride weighing 3.0360 g is dissolved in a 500-ml volumetric flask. To 25.00 ml of the solution 50.00 ml of a $0.0847N$ solution of $AgNO_3$ are added. The amount of NH_4SCN ($T_{NH_4SCN/Ag} = 0.01165$) spent for the titration of excess $AgNO_3$ is 20.68 ml. Calculate the percentage of potassium chloride in the sample.

17. A sample of common salt weighing 0.1160 g is dissolved in water and treated with 40.00 ml of a $0.09540N$ solution of $AgNO_3$. If 19.35 ml of ammonium thiocyanide ($K = 1.0500$ for $0.1N$) are spent for the titration of the solution, calculate the percentage of NaCl in the sample.

18. A sample of a mixture of chlorides weighing 0.1730 g is dissolved and treated with 50.00 ml of $AgNO_3$ ($T = 0.01721$). The amount of ammonium thiocyanide ($K = 0.8532$ for $0.05N$) spent for the titration of excess silver is 56.40 ml. Calculate the percentage of chlorine in the mixture.

19. A sample of a substance containing sulphuric acid and weighing 3.9770 g is dissolved in a 250-ml volumetric flask. If 25.00 ml of the solution are precipitated with 25.00 ml of barium chloride solution and 32.25 ml of $K_2Cr_2O_7$ solution ($T = 0.01252$) are spent for the titration of excess barium chloride, calculate the H_2SO_4 content of the sample, when 20.00 ml of barium chloride are equivalent to 26.63 ml of potassium dichromate.

20. A sample of a sulphur compound weighing 4.1650 g is dissolved in water and the solution is diluted in a 250-ml volumetric flask. We then treat 20.00 ml of the solution with 20.00 ml of $BaCl_2$ solution. Excess Ba^{2+} ions are titrated with 24.20 ml of a 0.02677*N* solution of $K_2Cr_2O_7$ (oxidant). The titration establishes that 1.00 ml of $BaCl_2$ is equivalent to 1.27 ml of potassium dichromate. Calculate the percentage of free sulphuric acid in the sample.

21. A sample of sodium bromide weighing 0.2058 g was dissolved in water for testing for purity. The solution was treated with 40.00 ml of an $AgNO_3$ solution with a concentration of 0.0998*N*. The amount of an ammonium thiocyanide solution spent for the back titration of excess silver was 21.20 ml. Calculate the percentage of impurities in the sample if 1.00 ml of the $AgNO_3$ solution is equivalent to 1.06 ml of the NH_4SCN solution.

22. A sample of soda weighing 2.1010 g is dissolved, acidified with nitric acid, and treated with 5.00 ml of an $AgNO_3$ solution ($K = 1.0220$ for 0.1*N*). The amount of an ammonium thiocyanide solution ($T = 0.007598$) spent for the titration of excess $AgNO_3$ is 2.40 ml. Calculate the NaCl content of the sample.

23. A sample of liquid taken from a carbonization column during the manufacture of soda is tested for Cl^- ion. We dilute 10.00 ml of the sample with water in a 500-ml volumetric flask, and then 10.00 ml of the diluted solution are acidified with HNO_3 and treated with 20.00 ml of a 0.09854*N* solution of $AgNO_3$. The amount of ammonium thiocyanide ($T_{NH_4SCN/AgNO_3} = 0.01699$) spent for the titration of excess $AgNO_3$ is 15.20 ml. Calculate the number of grams of Cl^- ion contained in 1000 ml of the sample.

24. An almost saturated solution of table salt is used in the manufacture of soda. The solution is tested for chloride ion content. A 5.00 ml quantity of the salt solution is diluted with water in a 200-ml volumetric flask, and 20.00 ml of the diluted solution are acidified with nitric acid and treated with 30.00 ml of $AgNO_3$ ($T = 0.01679$). The amount of ammonium thiocyanide spent for the titration of excess silver is 9.86 ml. A separate titration establishes that 1.00 ml of ammonium thiocyanide is equivalent to 0.94 ml of silver nitrate. Determine the following: (a) the chloride

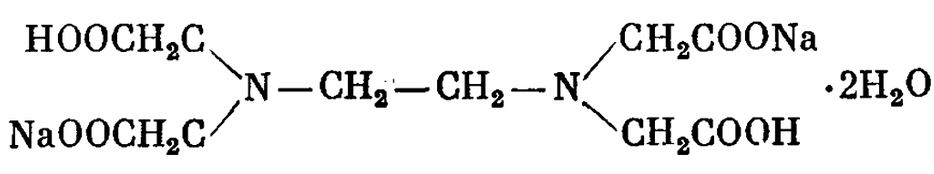
ion content, (b) the sodium chloride content of the sample (both in g/litre).

25. A sample of rock salt weighing 3.2680 g is dissolved in a 250-ml volumetric flask. If 10.00 ml of the obtained solution are treated with 20.00 ml of an $AgNO_3$ solution ($K = 1.0040$ for $0.1N$), and 2.12 ml of a $0.09950N$ solution of NH_4SCN are spent for the back titration of excess silver, calculate the percentage of (a) chloride ion, (b) NaCl in the sample.

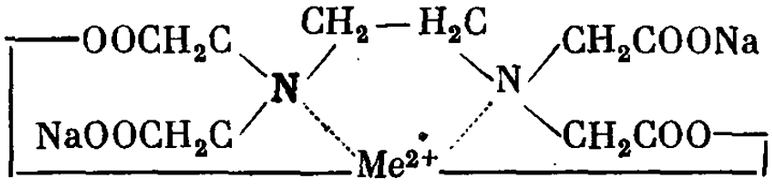
26. A sample of zinc white weighing 0.1624 g is taken for testing for ZnO content. A solution obtained by dissolving the sample is titrated with an excess quantity (22.40 ml) of potassium ferrocyanide. The amount of $ZnSO_4$ solution spent for the back titration of the excess potassium ferrocyanide is 2.82 ml. Calculate the percentage of ZnO in the sample if $T_{K_4Fe(CN)_6/Zn} = 0.006517$ and 1.00 ml of potassium ferrocyanide is equivalent to 1.08 ml of the $ZnSO_4$ solution.

C. Calculations in complexometric determinations

Some organic compounds that form stable complexes with various ions can successfully be used in titrimetric determinations. Such compounds are known as *complexones* and the method using standard complexone solutions is called complexometric. This method is widely used in practical analysis of chemical substances. Complexones are alpha-amino acids whose molecules contain a nitrogen atom bound with methylcarboxyl groups. Disodium salt of ethylenediaminetetraacetic acid is commonly used for titrimetric determinations. The salt is known in the literature as Trilon B, EDTA, Chelaton III, Complexone III, etc. The first two names are the most widely used among chemists. The molecule of this compound has the following structure:



The ions of many metals form stable inner complex compounds with EDTA:



A gram-equivalent of EDTA is equal to half its molecular weight. The most commonly used concentrations of the reagent are 0.1 or 0.05*N*. The titrimetric method based on the use of this substance is known as the *trilonometric* method.

Various substances are used as indicators in trilonometric determinations, the selection of which depends on the desired ion. Murexide, $C_8H_5O_6N_6 \cdot H_2O$ (ammonium purpurate) is suitable for the determination of calcium (as well as Ni, Co, Cu). Eriochrome black T (chromogene, special, ETOO) is used for the determination of magnesium. Other indicators are also used.

Trilon B standard solution is usually standardized against a solution prepared by dissolving a salt of the desired cation, with strict coherence to the conditions that all stages of the determination are carried out under identical conditions, particularly with regard to the concentration of solutions, the amounts of indicators added, and the pH of solutions. The calculations involved in trilonometric determinations do not differ from those used in all the other titrimetric methods described above.

Problems

1. What quantity of Trilon B, in grams, is required to prepare 250 ml of a 0.05*N* solution?
2. Calculate the mass of Trilon B required to prepare 2.5 litres of an approximately 0.1*N* standard solution.
3. What quantity, in grams, of Trilon B is required to prepare 250 ml of a standard solution intended for the determination of calcium in a solution containing about 1 g/litre of calcium?
4. What quantity, in grams, of Trilon B is required to prepare 200 ml of a solution for the determination of mag-

nesium in a mineral containing about 15 per cent of magnesium? It is understood that a sample weighing 1 g is dissolved and the solution, after separation of interfering components, is diluted with water in a 500-ml volumetric flask.

5. A sample of dry pure $CaCO_3$ weighing 1.3250 g is dissolved in a 250-ml volumetric flask in order to standardize a working solution of Trilon B. The amount of Trilon B solution spent for the titration of 25.00 ml of the solution (after the appropriate treatment and dilution) is 26.47 ml. Determine the normality and the titre on the Trilon B solution against calcium.

6. To titrate 20.00 ml of a solution prepared by dissolving 1.5250 g of anhydrous pure $MgSO_4$ in a 500-ml volumetric flask 19.55 ml of Trilon B solution are used. Determine the normality and the titre of the Trilon B solution against magnesium.

7. To determine the total hardness of water, a 0.05*N* solution of Trilon B is prepared and standardized against a standard solution in which [Ca] and [Mg] are in the proportion of 3:1. The standard solution is prepared as follows. Pure $CaCO_3$ and $MgSO_4$ (anhydrous) are dissolved in separate 500-ml volumetric flasks. Then, 75 ml of the first solution (containing Ca^{2+} ion) are placed in a 250-ml volumetric flask, with 25 ml of the second solution then being added. The mixture is then diluted with double-distilled water to the mark. Calculate the masses of the $CaCO_3$ and $MgSO_4$ samples which are required for this analysis.

8. Determine the normality of a standard solution obtained by dissolving 3.0000 g of $MgSO_4$ (anhydrous) and 2.5000 g of $CaCO_3$ in 500-ml volumetric flasks, if 25 ml of the first solution are then mixed with 75 ml of the second in a 200-ml volumetric flask and the mixture is diluted with water added to the mark.

9. A sample of dolomite weighing 2.0250 g is dissolved, the insoluble residue and sesquioxides are separated, and the filtrate placed in a 500-ml volumetric flask and diluted with water to the mark. The amount of a 0.1025*N* solution of Trilon B spent for the titration of 25.00 ml of this solution after dilution with water and the appropriate treatment (neutralization, addition of indicator and buffer

solution) is 20.20 ml. Another 100.0 ml of the same solution are taken from the flask and Ca^{2+} is precipitated quantitatively. The filtrate (after the appropriate treatment) is titrated with 38.50 ml of the same standard solution of Trilon B. Calculate the CaO and MgO contents of the sample.

10. A sample of a mineral weighing 2.0850 g is treated to separate the interfering components, dissolved, and diluted with water to the mark in a 250-ml volumetric flask. The solution is used for the determination of calcium and magnesium in the sample. Two aliquots, of 25.00 and 100.00 ml, are placed in flasks for titration. The amount of a standard solution of Trilon B (0.05240*N*) spent for the titration of the first aliquot is 11.20 ml and of the second (after quantitative separation of Ca^{2+}), 21.65 ml. Calculate the percentage of Ca and Mg in the sample.

11. A sample of carbonate rock weighing 0.5126 g was dissolved in hydrochloric acid and the insoluble residue and sesquioxides were separated. The solution was placed in a 250-ml volumetric flask and water added to the mark. To titrate 50.00 ml of this solution (after the addition of water, a buffer solution, and an indicator), 20.42 ml of a 0.1012*N* solution of Trilon B were spent. The amount of the same standard solution spent for the titration of 100.0 ml of the same solution, after separation of calcium, was 19.62 ml. Determine the percentage of CaO and MgO in the sample.

12. When the total hardness of a water sample was determined, 24.18 ml of Trilon B solution ($K = 1.054$ against 0.01*N*) were spent to titrate 50.00 ml of the water (in the appropriate conditions). The amount of the same Trilon B solution spent for the titration of 25.00 ml of the same solution, in the presence of murexide mixture as an indicator, was 10.10 ml. Determine the hardness of the water due to magnesium, expressing it in mg/litre of Mg^{2+} and in mg-equiv/litre.

INTRODUCTION

1. (b), (d), (e) accurate; the others are approximate. **2.** An accurate number, valency. **3.** The number (c) is accurate, the others are approximate. **4.** Accurate numbers are (a) and (d); (b) and (c) are approximate. **5.** 8 g; 8.00 g; 8.0000 g. **6.** 10 ml; 10.0 ml; 10.00 ml. **7.** 25.935; 25.94; 25.9; 26. **8.** 0.9972 kg; 0.997 kg; 1.0 kg. **9.** (a) 6 significant figures and 4 decimal places; (b) 2 significant figures and 4 decimal places; (c) 4 or 6 significant figures (depending on the accuracy of the number) and 3 decimal places. **10.** (a) one significant figure; no decimal places; (b) 4 significant figures and 4 decimal places; (c) 2 significant figures and 4 decimals; (d) 4 significant figures and 3 decimal places; **11.** 1.7 g; 1.6667 g. **12.** 8.3 cm. **15.** 3.1 g. **16.** 2480.7. **17.** 0.15. **18.** 12.2% **19.** $\frac{0.98 \times 24 \times 56 \times 500}{25 \times 1000 \times 0.9} \approx 30$. **20.** $\frac{258 \times 0.001 \times 18 \times 0.45}{300 \times 0.0091} \approx 0.77$ **21.** 0.5314. **22.** 0.053358. **23.** (a) Slide rule; (b) four-place tables of logarithms. **24.** (a) Slide rule; (b) five-place table of logarithms. **25.** 0.0029 mole of anhydrous salt. **26.** 1×10^{22}. **27.** (a) about 6%; (b) 5.687%. **28.** (a) 36%; (b) 36.077%.

CHAPTER ONE

GENERAL THEORETICAL PRINCIPLES OF ANALYTICAL CHEMISTRY

A. Concentration of Solutions

1. 60 g. **2.** 160 g. **3.** 15%. **4.** 13%. **5.** 9.6%. **6.** 12.9%. **7.** 228 g. **8.** 56 ml. **9.** 235 g. **10.** 83 g; 417 g. **11.** 154.6 g. **12.** 93 g. **13.** 6.3 g. **14.** 80.9 g. **15.** 14 g; 236 g. **16.** 263 g. **17.** 13.95 g. **18.** 0.45 g; 0.94 g; 1.76 g. **19.** 0.17%. **20.** 34.8%. **21.** 0.39%. **22.** 10.2%. **23.** ~14%. **24.** 9.1%. **25.** 8.5%. **26.** 9.1%. **27.** 11.8%. **28.** 20%. **29.** (a) 49.04; (b) 98.08; (c) 49.04; 16.34; 12.26. **30.** (a) 63.01; (b) 63.01; 21.01; 7.88. **31.** (a) 17.05; (b) 17.05; 5.68; 4.26. **32.** (a) 32.03;

(b) 32.03; (c) 16.02. **33.** (a) 158.04 g; (b) 158.04 g; 52.68 g; 31.61 g. **34.** (a) 97.11; (b) 64.74. **35.** (a) 482.19 g; (b) 160.73 g; (c) 120.55 g. **36.** (a) 54.07 g; (b) 162.21 g. **37.** (a) 147.10 g; (b) 49.03 g. **38.** (a) 139.01 g; (b) 278.02 g. **39.** (a) 196.07; (b) 196.07; (c) 392.14. **40.** $^1/_2M$; $^1/_6M$; $^1/_2M$; $^1/_6M$. **41.** (a) 63.03; (b) 63.03. **42.** (a) 94.80 g; (b) 94.80 g. **43.** 0.0500M; 0.100N. **44.** (a) 0.2000M; (b) 0.6000N; 0.4000N; 0.2000N. **45.** 0.125M; 0.250N. **46.** 0.200M; 0.400N. **47.** (a) 2.33M; 4.65N; (b) 8.75M; 8.75N; (c) 4.34M; 4.34N. **48.** (a) 35.94N; (b) 14.88N; (c) 12.39N. **49.** 12.82N. **50.** (a) 2.02M; (b) 6.06N; 4.04N; 2.02N. **51.** 0.004904 g. **52.** 0.0365 g. **53.** 0.125 g. **54.** 0.00072g. **55.** 46 mg. **56.** 17.7 mg. **57.** 28.4%. **58.** 19.9%. **59.** (a) 25%; (b) 31.8%; (c) 34.5%. **60.** 6.02%; 0.63M. **61.** 2.0 g. **62.** 2.65 g. **63.** 2.38 g. **64.** 240 g. **65.** 22.4 lit. **66.** 280 ml. **67.** 0.1M; ~0.2N. **68.** 1.6M; 3.2N. **69.** 101 g. **70.** 168 g. **71.** 564.4 g. **72.** 5.63 g. **73.** 144 ml. **74.** 114 ml. **75.** 334 ml. **76.** 78 ml. **77.** 84 ml. **78.** 84 ml. **79.** 6.4 lit. **80.** 1.8 lit. **81.** 404 ml. **82.** 840.7 ml. **83.** (a) 711 g; (b) 237 g; (c) 178 g. **84.** (a) 196 g; (b) 196 g; (c) 98 g. **85.** (a) 79 g; (b) 26 g; (c) 16 g. **86.** (a) 73.6 g; (b) 24.5 g. **87.** (a) 0.05N; 0.15N; 0.2N; (b) 0.05N. **88.** (a) 2N; (b) 6N; (c) 16N. **89.** 0.0147 mole/litre. **90.** 9.9×10^{-6} mole/litre. **91.** $1.05 \times 10^{-5}M$. **92.** $1.5 \times 10^{-4}M$. **93.** $3.6 \times 10^{-2}M$; $1.1 \times 10^{-4}M$; $6.2 \times 10^{-4}M$; $5 \times 10^{-7}M$. **94.** $1 \times \times 10^{-6}M$; $1.2 \times 10^{-4}M$; $1 \times 10^{-8}M$. **95.** 0.025N; 0.1N. **96.** 0.33N; 0.17N; 0.10N. **97.** 0.42M; 0.083M. **98.** 0.24M; 0.16M. **99.** $7.3 \times \times 10^{-3}$ g-ion/litre; 5×10^{-2} g-ion/litre. **100.** 0.012 g-ion/litre; 0.0098 g-ion/litre. **101.** 5 : 23 or 1 : 4.6. **102.** 5 : 14 or 1 : 1.28. **103.** 2 : 1. **104.** 7 : 5. **105.** 263 g, 96% and 737 g, 20%. **106.** 400 g and 1600 g. **107.** 231 g and 769 g. **108.** 1 kg and 3 kg. **109.** 667 g. **110.** Add 300 g of 10% acid. **111.** 501 and 102 ml. **112.** 1435 ml and 83 ml. **113.** 12 : 50. **114** 3 : 2. **115.** 444 and 556 g. **116.** 3 kg H_2O and 2 kg of NH_3. **117.** 600 g. **118.** 116 g. **119.** 3 litres. **120.** 78.9 g. **121.** 346 ml. **122.** 1321 ml. **123.** 888 ml H_2O and 119 ml 60% acid. **124.** Mix 3 kg of acid and 7 litres of water. **125.** Dissolve 76.2 g of acid in 167.6 g of H_2O. **126.** 559 ml H_2O and 439 NH_3. **127.** 4.82 litres of water and 176 ml of acid. **128.** 2.54%. **129.** 4.31%. **130.** 313 ml of 50% and 196 ml of 20% solution. **131.** 1 : 4. **132.** 1 : 2. **133.** 1 : 19. **134.** 1 : 3. **135.** 100 ml of 6N and 400 ml of 1N solution. **136.** 400 ml of 2N and 1400 ml of 0.2N solution. **137.** 600 ml. **138.** 9.09 ml. **139.** 250 ml. **140.** 1190 ml. **141.** 0.92 litres of NH_3 and 2.08 litres of water. **142.** 0.125 litre of acid and 4.875 litres of water. **143.** 306 ml of water and 194 ml of acid. **144.** 1016 ml. **145.** 2.338 g. **146.** 4.659 g. **147.** 0.4679N. **148.** 0.08939N. **149.** 0.2514N. **150.** 1.982 g.

B. Chemical Equilibrium

3. Doubles. **4.** Increases 1.5 times. **5.** Increases 9 times. **6.** Increases 48 times. **7.** Decreases two times. **8.** Doubles. **9.** Reverse. **10.** Reverse. **11.** Will not produce any effect. **12.** Will shift to the right. **13.** $K = 9$. **14.** $K = 1.3$. **15.** $K = 6.9$. **16.** $K = 3.37$. **17.** $K' > K''$ four times. **18.** $K'' > K'$ 1.25 times. **19.** [CO] = 1.5 moles/litre; [Cl_2] = 1.0 mole/litre. **20.** [A] = 0.95 mole/litre; [B] =

= 0.75 mole/litre. 21. 1.3*M*. 22. 60%. 24. [HCl] = 0.91; 1.50; 1.74; 1.83 moles/litre; further increase is unfavourable. 25. Decreases 1.2 times. 26. 70%. 27. [CO] = $[H_2O]$ = 0.067 mole/litre; $[CO_2]$ = = 0.03 mole/litre; $[H_2]$ = 0.13 mole/litre. 28. 0.75 mole/litre. 29. 92%. 30. 88%.

C. Ionic Equilibrium

1. 1 g-ion H^+ and 1 g-ion Cl^-. 2. 2 g-ions Na^+ and 2 g-ions Cl^-. 3. 2 g-ions H^+ and 1 g-ion SO_4^{2-}. 4. 1 g-ion Ba^{2+} and 2 g-ions OH^-. 5. 0.02 g-ion Al^{3+} and 0.03 g-ion SO_4^{2-}. 6. 1.5 g-ion Na^+ and 0.5 g-ion PO_4^{3-}. 7. 0.5 mole $BaCl_2$. 8. 0.02 mole $PbCl_2$. 9. 0.1 mole H_3PO_4. 10. 0.2 mole $Ca_3(PO_4)_2$. 11. 0.78 or 78%. 12. 0.4 or 40%. 13. 0.9 or 90%. 14. 0.004 or 0.4%. 15. About 0.003 g-ion/litre. 16. $1.24 \times$ $\times 10^{-4}$ g-ion/litre. 17. 9×10^{-3}; 1.3×10^{-4} g. 18. 0.39 g; 13.85 g; 4.02 g. 19. 13.8 g. 20. CH_3COOH; about 200 times as much. 21. 3.43×10^{-4} g; 2.5×10^{-6} g-ion. 22. (a) 0.023 g-ion/litre; 0.92 g/litre; (b) 0.014 g-ion/litre, 0.56 g/litre; (c) 1.3×10^{-4} g-ion/litre and $5.2 \times$ $\times 10^{-3}$ g/litre. 27. 1.8×10^{-5}. 28. 2.1×10^{-4}. 29. 4.7×10^{-4}. 30. 5×10^{-10}. 31. 4×10^{-7}. 32. 5.6×10^{-8}. 33. Obeys. 34. Does not obey. 35. 1.8×10^{-5}. 36. Variable. 37. 3.3×10^{-3} g-ion/litre. 38. 9.5×10^{-3} g-ion/litre. 39. Decreases 2.2 times. 40. Decreases about two times. 41. 2.4×10^{-3} g; 0.1 g. 42. 1.6×10^{-3} g. 43. 4.2%. 44. Increases 3.2 times. 45. 0.02%; 2.8×10^{-2}%; 6.3×10^{-2}%. 46. 0.1%; 10^{-5}%. 47. 1.9%; 3%; 4.2%, 4.7%; 13%. 49. $3.54 \times$ $\times 10^{-4}$ g-ion/litre. 50. 3.7×10^{-4} g-ion/litre. 51. 1.86×10^{-5} g-ion/litre. 52. 1.3×10^{-4} g-ion/litre. 53. 0.18%. 54. 0.0186%. 55. About ten times. 56. Decreases about 11 times. 57. 0.04%. 58. 0.51%. 59. 0.037*M*. 60. 0.3 g.

D. Equilibrium in Saturated Solutions

5. 0.00092 mole/litre. 6. 1.4×10^{-4} mole/litre. 7. 1.3×10^{-5} mole/litre. 8. 6.2×10^{-4} mole/litre. 9. 1.1×10^{-5} g-ion/litre. 10. $1.5 \times$ $\times 10^{-2}$ g-ion/litre. 11. 0.15 g-ion/litre. 12. 1.3×10^{-4} g-ion/litre 13. 0.98×10^{-10}. 14. 1.7×10^{-8}. 15. 1.01×10^{-5}. 16. 1.69×10^{-10}. 17. 1.64×10^{-5}. 18. 1.9×10^{-2}. 19. 4.3×10^{-17}. 20. 6.24×10^{-6}. 21. 4×10^{-29}. 22. 8.2×10^{-12}. 23. Saturated. 24. Unsaturated. 25. Supersaturated. 26. Will not. 27. Supersaturated. 28. Unsaturated. 29. Supersaturated. 30. Unsaturated. 31. 7×10^{-5} g-ion/litre 32. 7.9×10^{-3} g-ion/litre. 33. 1×10^{-5} g-ion/litre. 34. AgI—$9.2 \times$ $\times 10^{-9}$ g-ion/litre; AgBr—5.8×10^{-7} g-ion/litre; AgCl—1.3×10^{-5} g-ion/litre. 35. $[Pb^{2+}] = 1.6 \times 10^{-2}$ g-ion/litre; $[Cl^-] = 3.2 \times 10^{-2}$ g-ion/litre. 36. $[CrO_4^{2-}] = 7.9 \times 10^{-5}$ g-ion/litre; $[Ag^+] = 1.6 \times 10^{-4}$ g-ion/litre. 37. 1.3×10^{-4} g/100. 38. 0.10 g/100 H_2O. 39. 0.45 g. 40. 1.7×10^{-3} g. 41. In $PbCl_2$, about 2500 times. 42. In $PbSO_4$, about 260 times. 43. $Zn(OH)_2$; 160 times. 44. In CuS, 5.8×10^{-19}; in As_2S_3, 7.9×10^{-6} g. 45. Does not precipitate. 46. Does not precipitate. 47. Precipitates. 48. Does not precipitate. 49. Does not precipitate. 50. Precipitates. 51. Will precipitate. 52. Will precipi-

tate. 53. Will precipitate. 54. Will precipitate. 55. Will precipitate. 56. Precipitates. 57. $[Sr^{2+}] : [Ba^{2+}] = 3600 : 1$. 58. $10^6 : 1$. 59. AgBr. 60. $PbCrO_4$. 61. $[Ca^{2+}]$, 18 times. 62. $[C_2O_4^{2-}]$, 1900 times. 63. Br^-. 64. $BaCrO_4$. 65. 8×10^{-6} g-ion/litre. 66. 2.3×10^{-2} g-ion/litre. 67. $SrCO_3$. 68. $BaSO_4$, then $CaSO_4$. 69. 0.13 mole/litre. 70. 2.9×10^{-4} mole/litre. 71. $> 1.6 \times 10^{-4}$ mole/litre. 72. Any soluble sulphate; $> 0.6 \times 10^{-4}$ mole/litre. 73. Any soluble carbonate; $1.6 \times$ $\times 10^{-6}$ mole/litre. 75. 5.7×10^{-7} g-ion/litre. 76. 1.8×10^{-6} g-ion/litre. 77. CuS. 78. CdS. 79. Cannot. 80. Can. 81. $[Cd^{2+}]$, 1.8 times greater. 82. $[Sn^{2+}]$, 15 times greater. 83. 0.12 g-ion/litre. 84. 0.95 g-ion/litre. 85. Practically impossible. 86. 0.33 g-ion/litre. 87. 0.01-0.12 g-ion/litre. 88. Pb^{2+} and Cu^{2+}. 89. ZnS and CdS. 90. Cd^{2+} and Cu^{2+}.

E. Complex Compounds

17. 1.3×10^5 times greater in $K[AgCl_2]$ solution. 18. In ammoniate. 19. In ammoniate. 20. In ferrocyanide. 21. $[Ag^+] = 1.2 \times 10^{-3}$ g-ion/litre; $[NH_3] = 2.4 \times 10^{-3}$ mole/litre. 22. $[Ag^+] = 8.3 \times 10^{-3}$ g-ion/litre; $[Cl^-] = 1.7 \times 10^{-2}$ g-ion/litre. 23. In ammoniate. 24. Decreases 2×10^4 times 25. Precipitate falls out. 26. Will precipitate.

CHAPTER TWO

GRAVIMETRIC ANALYSIS

A. Weighing on a Balance

1. 10.1 2. 9.6. 3. To the left. 4. To the right. 5. Yes. 6. No. 7. + 0.0066. 8. —0.0044. 13. 0.0084. 14. 0.0024. 15. 0.3 mg. 16. (a) 0.91 mg; (b) 1.1 divisions. 17. 20.9940 g. 18. 5.4968 g. 19. 9.9902 g. 21. 6.3243 g. 22. 7.2863 g. 23. 6.8939 g. 24. 12.4965 g. 25. 12.4554 g. 26. 31.4810 g. 27. Right-hand one, 0.002 mm longer. 28. By 0.0032 mm. 29. 0.001%; 0.2%. 30. 0.0005 g. 33. 68.5828 g. 34. 7.0932 g. 35. 10.7995 g. 36. 0.9095 g.

B. Calculating the Mass of a Sample

1. ~0.7 g. 2. ~0.5 g. 3. ~1 g. 4. ~0.2 g. 5. ~0.3 g. 6. ~0.2 g. 7. ~0.2 g. 8. ~0.2 g. 9. ~0.7 g. 10. ~0.3 g. 11. ~0.2 g 12. ~2.5 g. 13. ~0.5 g. 14. ~3 g. (normal precipitate, 0.01 g). 15. ~1 g. 16. ~0.2 g. 17. ~0.4 g. 18. ~0.3 g. 19. ~0.8 g. 20. ~0.5 g. 21. ~0.07 g. 22. ~0.1 g. 23. ~0.3 g. 24. ~0.2 g. 25. ~0.1 g. 26. ~0.1 g. 27. ~0.1 g. 28. ~0.1 g. 29. ~3 g.

30. ~0.02 g. 31. ~0.2 g. 32. ~0.2 g. 33. ~0.3 g. 34. ~0.2 g. 35. ~0.1 g. 36. ~0.4 g. 37. ~0.6 g. 38. ~0.4 g. 39. ~0.2 g. 40. ~0.4 g. 41. ~0.4 g. 42. ~0.6 g. 45. ~0.1 g Au; ~1.7 g Ag; ~1.3 g Cu. 46. ~0.2 g.

C. Calculating the Amounts of Solvent and Precipitating Agent

Note: Since effective excesses of solvent and precipitating agent, as well as amounts of precipitate, are strictly definite, the results obtained may differ significantly from the answers given.

1. ~40 ml. 2. ~60 ml. 3. ~15 ml. 4. ~2 ml. 5. ~1 ml. 6. ~60 ml. 7. ~90 ml**. 8. ~300 ml*. 9. ~8 ml**. 10. ~130 ml**. 11. ~6 ml**. 12. ~30 ml**. 13. ~15 ml**. 14. ~20 ml**. 15. ~15 ml**. 16. ~8 ml***. 17. ~100 ml**. 18. ~80 ml**. 19. ~20 ml. 20. ~10 ml. 21. ~20 ml**. 22. ~20 mm***. 23. ~4 ml*. 24. ~10 ml**. 25. ~8 ml*. 26. ~120 ml**. 27. ~60 ml. 28. ~5 g*. 29. ~0.5 g**. 30. ~0.9 g*. 31. ~30 ml. 32. ~6 ml*. 33. ~4 ml***. 34. ~10 ml***. 35. ~8 ml***. 36. ~9 ml*. 37. ~2 ml***. 38. ~4 ml***. 39. ~2 ml**. 40. ~6 ml*. 41. ~4 ml***. 42. ~1 ml**.

D. Calculating the Loss in Precipitate Washing

1. 5.8×10^{-4} g. 2. 4.5×10^{-3} g. 3. 1.1×10^{-3} g. 4. 0.11 g. 5. $1.4 \times \times 10^{-3}$ g. 6. 5.3×10^{-4} g. 7. 0.6%. 8. 1.8%. 9. 1.4%. 10. 5.4%. 11. 6.2%. 12. 3.8%. 13. 3.6%. 14. 0.16%. 15. 1.2×10^{-6} g. 16. 2.9×10^{-5} g. 17. 2.8×10^{-6} g. 18. 3.5×10^{-7} g. 19. 2×10^{-3}%. 20. 0.02%. 21. 400 times greater. 22. 0.6 ml.

F. Calculating the Results of Gravimetric Analysis

1. 41.73%. 2. 3.28%. 3. 72.40%. 4. 3.16%. 5. 39.77%. 6. 43.98% CO_2; 56.04% CaO. 7. 25.10%. 8. 59.96%. 9. 88.51%. 10. 14.80%. 11. 3.01%. 12. 19.99%. 13. (a) 1.95%; (b) 3.02%. 14. (a) 0.38%: (b) 50.19%. 15. 78.71%. 16. 1.01%. 17. 39.90%. 18. 39.49%. 19. 0.2804 g. 20. 0.03921 g. 21. 0.2749 g. 22. 0.09034 g. 23. 0.8161 g. 24. 0.04729 g. 25. (a) 0.1110 g; (b) 0.1382 g; (c) 0.4883 g. 26. (a) 0.1156 g; (b) 0.3143 g; (c) 0.5752 g. 27. (a) 0.0509 g; (b) 0.1166 g; (c) 0.2549 g. 28. (a) 0.01802 g; (b) 0.02170 g; (c) 0.04015 g. 29. 1.9224 g. 30. 1.7426 g. 31. 56.09%. 32. 3.92%. 33. 34.56%. 34. 22.24%. 35. 90.01%. 36. 94.85%. 37. (a) 0.97%; (b) 30.92%; (c) 1.28%. 38. 11.51%. 39. (a) 29.32%; (b) 0.32%; (c) 70.36%. 40. (a) 75.98%; (b) 2.13%. 41. (a) 19.67%; (b) 32.62%; (c) 68.22%.

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* At 50% excess of solvent
** At 100% excess of solvent
*** At 200% excess of solvent

42. (a) 9.86%; (b) 25.43%. 43. 98.68%. 44. 94.92%. 45. 74.34%. 46. 98.57%. 47. (a) 57.27%; (b) 81.89%. 48. (a) 46.01%; (b) 59.19%. 49. (a) 72.67%; (b) 52.58%. 50. Pure. 51. 56.21%. 52. 77.05%. 53. 79.24%. 54. 14.58%. 55. 14.80%. 56. 22.14%. 57. 8.12%. 58. 15.22%. 59. 37.25%. 60. 0.09%. 61. 0.0164 g. 62. 13.51%. 63. 92.47%. 64. 12.06%. 65. 3.07%. 66. (a) 20.40%; (b) 46.75%. 67. 0.59% 68. (a) 55.11%; (b) 34.81%. 69. (a) 2.00%; (b) 0.998%. 70. Pure. 71. 56.03%. 72. 1.7847 g. 73. 0.2185 g. 74. 0.2783 g. 75. 1.119 g. 76. 0.1723 g. 78. 0.1196 g. 79. 0.5460 g. 80. 1.2361 g. 81. 0.2690 g. 82. 0.1112 g. 83. 86.98%. 84. 0.07%. 85. 0.2235 g. 86. 0.08821 g. 87. 1.0326 g. 88. 0.06208 g. 89. No. 90. Correct. 91. Non-magnesium sulphates. 92. Non-calcium carbonates. 93. 60.51%. Excess moisture. 94. 35.81%. 95. 16.94%. 96. 47.24%. 97. (a) 1.77%; (b) 5.86%. 98. 1.63%. 99. 1.45%. 100. 82.34%.

G. Calculations Involving the Removal or Introduction of a Component

1. 54.89%. 2. 22.11%. 3. 9.55%. 4. 68.55%. 5. 87.57% CaO; 10.66% MgO; 0.99% ($Al_2O_3 + Fe_2O_3$); 0.81% SiO_2. 6. 49.60% SiO_2. 7. 41.36% MgO. 8. 46.86% CO_2. 9. 65.94% Ba; 34.05% Cl. 10. 39.85% SO_4^{2-}; 72.23% SO_4^{2-}; 11.58% Fe^{3+}; 20.99% Fe^{3+}. 11. 37.22%; 38.76%. 12. (a) 24.04%; (b) 38.26%. 13. 11.58% H_2O; 67.34% CaO; 16.38% MgO; 3.54% SiO_2; 1.21% CO_2. 14. 52.71% CaO; 37.71% CO_2; 2.02% sesquioxides; 0.69% SiO_2. 15. 7.15%. 16. 10.17%. 17. 82.45% CaO; 11.26% MgO; 4.33% SiO_2; 1.48% sesquioxides. 18. 28.41% Fe_2O_3; 42.74% SO_3. 19. 7.33%. 20. 2.13 roubles.

I. Indirect Determinations

1. 65% $BaCO_3$; 35% $CaCO_3$. 2. 72.83% NH_4Br; 27.17% KBr. 3. 0.1368 g KCl; 0.07518 g Kl. 4. 0.0830 g NaCl; 0.09673 g NaBr. 5. 79.04% NaCl; 20.96% KCl; 6. 21.74% NaCl; 78.26% NaBr. 7. 43.57% $MgCO_3$; 56.43% $CaCO_3$. 8. 13% CaO; 37% MgO. 9. 32% NaCl; 48% KCl. 10. 11% Na_2O; 3.7% K_2O.

CHAPTER THREE

FUNDAMENTAL THEORY OF TITRIMETRIC (VOLUMETRIC) ANALYSIS

A. Calculation in Titrimetric Analysis

1. 96.53%. 2. 49.65%. 3. 0.1401 g. 4. 0.2011 g. 5. 0.4500 g. 6. 0.2280 g. 7. 250 ml. 8. 50 ml. 9. 0.0534 g excess acid. 10. 0.01962 g excess H_2SO_4. 11. 80.00%. 12. 98.08%. 13. 0.1*N*. 14. 0.2*N*. 15. 0.09130*N*.

16. 0.1640*N*. 17. 4 : 5. 18. 4 : 3. 19. 1.14 times. 20. 1.01 times. 21. 20 ml. 22. 37.50 ml. 23. 0.09868*N*. 24. 0.08724*N*. 25. 0.2245*N*. 26. 0.1217*N*. 27. 25 ml. 28. 400 ml. 29. Acid. 30. Acid.

B. Measuring Volumes

1. 997.17 g. 2. 997.94 g. 3. Greater than one litre. 4. The first. 5. 249.37 g. 6. 498.12 g. 7. 1.67 g. 8. 0.54 g. 9. 0.75 g. 10. 0.33 g. 11. 0.36 g. 12. 0.142 g. 13. 999.53 ml; —0.47 ml. 14. 500.37 ml; +0.37 ml. 15. 999.21 ml; —0.79 ml. 16. 499.80 ml; —0.20 ml. 17. 249.91 ml; —0.09 ml. 18. 200.30 ml; +0.30 ml. 19. 150.10 ml; +0.10 ml. 20. 99.92 ml; —0.08 ml. 21. 20.04 ml; +0.04 ml. 22. 25.00 ml. 23. 22.4 mm. 24. 42.93 mm above the lower mark. 25. 21.4 mm above the lower mark. 26. 54.1 mm above the lower mark; the capacity, 50 ml. 27. 13.3 mm above the upper mark; the capacity, 25 ml. 28. 10.3 mm above the upper mark; the capacity, 100 ml. 29. 29.99 ml; —0.01 ml.

C. Expressing the Concentration of a Standard Solution

1. 0.005912. 2. (a) 0.007652; (b) 0.003639. 3. (a) 0.005624; (b) 0.01276. 4. (a) 0.005416; (b) 0.003167. 5. (a) 0.05742 g; (b) 0.1436 g; (c) 0.5742 g. 6. (a) 0.04120 g; (b) 1.030 g; (c) 4.120 g. 7. 0.1958 g. 8. (a) 0.1472 g; (b) 0.06453 g. 9. 0.1012 g. 10. 0.07379 g. 11. 0.03647. 12. 0.05611. 13. 0.005856. 14. 0.005435. 15. 0.002503. 16. 0.002191. 17. 0.003647. 18. 0.005611. 19. 0.005106. 20. 0.002954. 21. 0.04106. 22. 0.04960. 23. 0.002341. 24. 0.003928. 25. 0.03874 g. 26. 0.1600 g. 27. 1.386 g. 28. 0.7262 g. 29. 0.4794 g. 30. 0.4020 g. 31. 0.005087. 32. 0.004335. 35. 1.000*N*. 36. 0.1000*N*. 37. 0.1010*N*. 38. 1018*N*. 39. 0.09705*N*. 40. 0.09406*N*. 41. 0.09273*N*. 42. 0.1036*N*. 43. (a) 0.03161*N*; (b) 0.09483*N*. 44. (a) 0.05657*N*; (b) 0.09428*N*. 45. 0.09502*N*. 46. 0.09960*N*. 47. 0.09798*N*. 48. 0.1037*N*. 53. 0.9399*N*. 54. 0.1437*N*. 55. 0.1040*N*. 56. 0.8941*N*. 57. 0.2185*N*. 58. 0.4971*N*. 59. 0.1875*N*. 60. 0.1947*N*; no. 61. 1.650 g; no. 62. 0.2666 g. 63. 0.9464*N*. 64. 0.2716*N*. 65. 2.162*N*. 66. 0.09989*N*. 67. 0.1000*N*. 68. 0.09885*N*. 69. 0.05067*N*; 0.03040*N*. 70. 0.2016*N*. 71. 1.124 for 0.1*N*. 72. 0.954 for 0.1*N*. 73. 0.972 for 0.05*N*. 74. 0.9900 for 0.02*N*. 75. 1.010 for 0.5*N*. 76. 1.006 for 0.2*N*. 77. 1.060 for 0.5*N*. 78. 0.9998 for 0.2*N*. 79. 0.9645 for 0.1*N*. 80. 1.037 for 0.5*N*. 81. 0.9905 for 0.2*N*. 82. 1.260 for 0.1*N*. 83. 0.004572. 84. 0.007907. 85. 0.002594. 86. 0.0004189. 87. 0.02196. 88. 0.0009698. 89. 0.5290*N*. 90. 0.1909*N*. 91. Alkaline. 92. Neutral. 93. NaOH. 94. KOH. 95. Alkaline. 96. Acid. 97. 0.1229 g. 98. 0.3361 g KOH. 99. 0.03404*N*. 100. 0.1425*N*. 101. 0.001794. 102. 0.001020.

CHAPTER FOUR

OXIDATION-REDUCTION METHODS

B. Permanganatometry

5. ~1.2 g. 6. ~9.5 g. 7. 2.021 g. 8. ~1.8 g. 9. ~16 g. 10. 1.264 g. 11. ~6.3 g. 12. ~1.34 g. 13. ~0.71 g. 14. ~0.17 g. 15. ~1.1 g. 16. ~0.50 g. 17. ~0.11 g. 18. ~0.08 g. 19. 0.18 g. 20. ~0.17 g. 21. No. 22. Yes. 23. (a) 0.007148; (b) 0.003180; (c) 0.1006*N*; (d) 1.006 for 0.1*N*. 24. (a) 0.003034; (b) 0.001522; (c) 0.04813*N*; (d) 0.9628 for 0.05*N*. 25. (a) 0.003537; (b) 0.001573; (c) 0.04978*N*; (d) 0.9956 for 0.05*N*. 26. (a) 0.003392; (b) 0.001600; (c) 0.05063*N*; (d) 1.0126 for 0.05*N*. 27. (a) 0.003180; (b) 0.004530; (c) 0.1006*N*; (d) 1.006 for 0.1*N*. 28. (a) 0.08800*N*; (b) 0.8800 for 0.1*N*; (c) 0.002782. 29. (a) 0.09891*N*; (b) 0.9891 for 0.1*N*; (c) 0.003126; (d) 0.005524. 30. (a) 0.08881*N*; (b) 0.8881 for 0.1*N*; (c) 0.01349. 31. (a) 0.002095; (b) 0.003701. 32. (a) 0.08938*N*; (b) 0.8938 for 0.1*N*; (c) 0.002825. 33. (a) 0.001571; (b) 0.04969*N*; (c) 0.9939 for 0.05*N*. 34. (a) 0.003092; (b) 0.09784*N*; (c) 0.9784 for 0.1*N*. 35. (a) 0.001616; (b) 0.05107*N*; (c) 1.022 for 0.05*N*. 36. 1.008 for 0.1*N*. 41. 19.13 ml. 42. 24.84 ml. 43. 23.47 ml. 44. 26.09 ml. 45. 21.36 ml; no. 46. 8.14 ml. 47. 21.64 ml. 48. 24.33 ml. 49. ~7.0 g. 50. ~0.84 g. 51. ~3.2 g. 52. ~3.7 g. 53. ~7.0 g. 54. ~1.4 g. 55. ~0.32 g. 56. ~1.4 g. 57. ~0.46 g. 58. ~0.70 g. 59. 0.7767 g. 60. 1.264 g. 61. 0.4200 g. 62. 6.522 g. 63. 0.1833 g. 64. 0.1237 g; no. 65. 0.2037 g. 66. 0.2961 g. 67. 0.1971 g. 68. 0.1928 g. 69. 0.08102 g. 70. 0.3388 g. 71. 0.2625 g. 72. 0.2803 g. 73. 97.06%. 74. 98.68%. 75. 98.32%. 76. 93.86%. 77. 42.27%. 78. 98.42%. 79. (a) 45.20%; (b) 90.43%. 80. 88.49%. 81. 28.63%. 82. 12.21%. 93. 92.20%. 84. 86.63%. 85. 89.34%. 86. 98.51%. 87. 92.42%. 88. 83.84%. 89. 90.65%. 90. 45.62%. 91. ~2 g. 92. ~2 g. 93. ~1 g. 94. ~7 g. 95. ~50 ml. 96. ~140 ml. 97. ~0.3 g. 98. ~0.3 g. 99. Yes. 100. Colourless. 101. 59.45%. 102. 56.00%. 103. 33.24%. 104. 98.31%. 105. 36.47%. 106. 71.20%. 107. 54.50%. 108. 99.88%. 109. 79.77%. 110. 50.19%.

C. Iodometry

1. ~1.6 g. 2. ~6,4 g. 3. ~37 g. 4. ~10 g. 5. ~ 2.5 g. 6. ~1 g. 7. ~0.06 g. 8. ~0.06 g. 9. No. 10. Yes. 11. Colourless. 12. No. 13. 0.001260 g. 14. 0.005048 g. 15. 0.04703*N*. 16. 0.04984*N*; 0.01237. 17. 0.1028*N*; 1.028 for 0.1*N*. 18. 0.01012*N*; 0.002512. 19. 0.02509. 20. (a) 0.02460; (b) 0.01258. 21. (a) 0.02833; (b)0.1142*N*; (c) 1.142 for 0.1*N*. 22. (a) 0.008888; (b) 0.03581*N*; (c) 0.7163 for 0.05*N*. 23. ~14 g. 24. ~1.4 g. 25. ~0.7 g. 26. ~0.2 g. 27. ~20 ml. 28. ~5 ml. 29. 92.96%. 30. 76.82%. 31. 38.10%. 32. 92.84%. 33. 98.29%. 34. 81.95%. 35. 18.51%. 36. 19.08%. 37. 90.42%. 38. 81.90%. 39. 35.35%. 40. 65.92%. 41. 32.87%. 42. 0.003766. 43. (a) 0.02224; (b) 0.1752*N*. 44. 93.98%. 45. 91.73%. 46. 32.64%.

47. 88.60%. **48.** 76.81%. **49.** 0.404%. **50.** 38.09%. **51.** 0.050%. **52.** 0.0035%. **53.** 0.02%. **54.** 0.038%. **55.** 0.80%. **56.** 0.53%. **57.** 1.04%. **58.** 1.37%. **59.** 3.61%. **60.** 0.59%. **61.** 94.00%. **62.** 1.66%. **63.** (a) 0.1020*N*; (b) 0.008143; (c) 0.006208. **64.** 19.08 ml. **65.** 1.85%. **66.** 60.81%.

CHAPTER FIVE

NEUTRALIZATION METHODS

A. Theoretical principles

11. 1×10^{0}; 1×10^{-1}; 1×10^{-3}; 1×10^{-6}. **15.** 9.2×10^{-2} g-ion/litre; 8.2×10^{-1} g-ion/litre. **17.** 1×10^{-11}; 1×10^{-10} g-ion/litre. **19.** 3. **21.** 2.7. **23.** 0.52; 13.48. **25.** 2.22; 11.78. **26.** 1.6; 12.4. **27.** 1.04; 12.96. **28.** 0.11; 13.89. **29.** 1.08; 12.92. **30.** 0.11; 13.89. **33.** 12.3. **34.** 12.3. **35.** 12.23. **36.** 11.7. **37.** 1.6; 12.4. **39.** 11.18; 2.82. **40.** 11.7; 2.3. **41.** 4.73. **45.** 0.0025 g-ion/litre. **49.** 0.016 g-ion/litre. **51.** $6.3 \times \times 10^{-3}$ g-ion/litre. **53.** 2.9. **54.** 2.9. **55.** 3.02; 0.001. **56.** 3.2; 0.00059. **57.** 2.47; 0.0034. **58.** 5.27; 5.4×10^{-6}. **59.** 10.86; 3.14. **60.** 11.5; 2.5. **61.** 5.27. **62.** 5 .5. **63.** 9. **64.** 5.8. **65.** 5.1. **66.** 5.3. **67.** 5.4. **68.** 5.2. **69.** 8.4. **70.** 9.1. **71.** 8.1. **72.** 10.9. **73.** 8.9. **74.** 8.2. **75.** 8.8. **76.** 8.5. **77.** 9.95. **78.** 9.25. **79.** 9.25. **80.** 8.77. **81.** 9.07. **82.** 9.19. **83.** 4.73. **84.** 3.75. **85.** 4.73. **86.** 3.87. **87.** 4.73. **88.** 5.32. **89.** 3.75. **90.** 4.90. **91.** 9.9. **92.** 8.98. **93.** (a) 1.17; (b) 1.96; (c) 7. **94.** (a) 12.8; (b) 12; (c) 7. **97.** (a) 4.25; (b) 4.73; (c) 5.20; (d) 8.87. **98.** (a) 2.79; (b) 3.75; (c) 4.24; (d) 8.0. **101.** 10.21; 9.63; 9.25; 8.29; 4.97.

B. Preparing Standard Solutions

1. ~1.7 g. **2.** ~4 g. **3.** ~109 ml. **4.** ~63 ml. **5.** ~32 ml. **6.** ~4.4 ml. **7.** ~10 g. **8.** ~0.53 g. **9.** ~0.59 g. **10.** 0.79 g. **11.** (a) 0.1876*N*; (b) 0.9380 for 0.2*N*; (c) 0.006841; (d) 0.007504. **12.** (a) 0.1065*N*; (b) 1.065 for 0.1*N*; (c) 0.005223; (d) 0.003300. **13.** (a) 0.1113*N*; (b) 1.113 for 0.1*N*; (c) 0.005458. **14.** (a) 0.1051*N*; (b) 1.051 for 0.1*N*; (c) 0.003833. **15.** (a) 0.09017*N*; (b) 0.9017 for 0.1*N*; (c) 0.003288. **16.** (a) 0.03884*N*; (b) 0.7767 for 0.05*N*; (c) 0.001905. **17.** (a) 0.01120; (b) 0.009135; (c) 1.142 for 0.2*N*. **18.** (a) 0.003720; (b) 0.004804; (c) 0.1020*N*. **19.** 0.003722. **20.** 0.002102. **21.** 1.007 for 0.1*N*. **22.** 1.042 for 0.05*N*. **23.** (a) 0.9340 for 0.1*N*; (b) 0.002895. **24.** (a) 0.1042*N*; (b) 0.005108. **25.** (a) 0.9688 for 0.1*N*; (b) 0.003879. **26.** (a) 0.08310*N*; (b) 0.003324. **27.** (a) 1.063 for 0.2*N*; (b) 0.007753. **28.** (a) 0.5136*N*; (b) 0.02054. **29.** ~0.8. **30.** ~1.1 g. **31.** ~3 g. **32.** ~1.7 ml. **33.** ~5.3 ml. **34.** ~3.8 g. **35.** ~11 g. **36.** ~9.4 g. **37.** ~0.6 g. **38.** ~0.32 g. **39.** ~1 g. **40.** ~2.5 g. **41.** ~2.3 g. **42.** ~1.4 g.

C. Calculating the Results of Analyses

1. 4.178 g. **2.** 6.122 g. **3.** 73.95%. **4.** 72.06%. **5.** 98.52%. **6.** 52.92%. **7.** 96.40%. **8.** 68.15%. **9.** 95.86%. **10.** 75.56%. **11.** 60.00%. **12.** 64.48%. **13.** 66.99%. **14.** 12.41*N*; 38.04%. **15.** 87.58%; 55.20%; 32.38%. **16.** 85.25%; 65.56%; 19.69%. **17.** 34.42%. **18.** 38.20%; 1.16% less. **23.** 0.09092*N*. **24.** 0.9070 for 0.1*N*. **25.** 0.09360*N*. **26.** 0.7344 for 0.5*N*. **27.** 99.59%. **28.** 54.20%. **29.** 90.19%. **30.** 31.22%. **31.** 16.87%. **32.** 4.047%. **33.** 92.10%. **34.** 16.81%; **35.** 31.86%. **36.** 17.92%. **37.** 99.77%; 43.87%. **38.** 1.23%. **39.** 29.27%. **40.** 67.41%; 63.12%. **41.** 90.40%; 9.38%. **42.** 88.69%; 10.34%. **43.** 82.49%; 17.48%. **44.** (a) 91.45; (b) 5.49%. **45.** 72.80% NaOH; 25.89% Na_2CO_3. **46.** 67.56%; 11.35%. **47.** 0.1987 g; 0.06145 g. **48.** 38.59%; 60.75%. **49.** 97.24%. **50.** 88.26%. **51.** 99.17%. **52.** 83.12%. **53.** 124.82 g/lit H_2SO_4; 238.91 g/lit H_3PO_4. **54.** 86.74 g/lit; 277.1 g/lit. **55.** 196.0 g/l; 32.77 g/l. **56.** 253.26 g/l; 78.73 g/l. **57.** (a) 2.69 mg-equiv/litre; (b) 7.55°. **58.** (a) 1.43 mg-equiv/litre; (b) 4.02°. **59.** (a) 2.16 mg-equiv/litre; (b) 10.81°. **60.** (a) 1.20 mg-equiv/litre; (b) 4.19°. **61.** (a) 12.20 mg-equiv/litre; (b) 34.21°. **62.** (a) 3.34°; (b) 13.78°; (c) 10.44°. **63.** (a) 1.94 mg-equiv/litre; (b) 5.45°; (c) 9.73°; (d) 6.80°. **64.** (a) 6.30 mg-equiv/litre; (b) 17.6°; (c) 31.5°; (d) 22.1°. **65.** (a) 19.99 g/litre; (b) 76.80 g/litre; (c) 56.81 g/litre. **66.** (a) 16.92 g/litre; (b) 55.72 g/litre; (c) 38.80 g/litre.

CHAPTER SIX

PRECIPITATION AND COMPLEXATION

A. Preliminary Calculations and Calculations Involving the Standardization of Solutions

1. ~2.1 g. **2.** ~26 g. **3.** ~2.16 g. **4.** 0.7022 g. **5.** ~3.7 g. **6.** ~0.73 g. **7.** ~0.15 g. **8.** ~0.073 g. **9.** ~3.8 g. **10.** ~2.9 g. **11.** 20.06 ml. **12.** 27.85 ml. **13.** 36.00 ml. **14.** No. **15.** 19.52 ml. **16.** 2.30 ml. **17.** 46.14 ml. **21.** ~1.8 g. **22.** ~1.8 g. **23.** ~60 g. **24.** ~3 g. **25.** ~0.22 g. **26.** ~0.074 g. **27.** ~0.07 g. **28.** ~0.3 g. **29.** ~3 g. **30.** ~0.4 g. **31.** 25.01 ml. **32.** 33.04 ml. **33.** 0.5474 g. **34.** 0.0695 g. **35.** 2.569 g. **36.** 0.5667 g. **37.** From 0.3 g to 0.6 g. **38.** From 0.136 g to 0.283 g. **39.** 0.007615. **40.** 0.08176*N*. **41.** (a) 0.04810*N*; (b) 0.9619 for 0.05*N*; (c) 0.008171. **42.** (a) 0.112*N*; (b) 1.121 for 0.1*N*; (c) 0.01210. **43.** (a) 0.04545*N*; (b) 0.9090 for 0.05*N*; (c) 0.001612. **44.** (a) 0.05078*N*; (b) 1.016 for 0.05*N*; (c) 0.004058. **45.** (a) 0.05484*N*; (b) 1.097 for 0.05*N*; (c) 0.004176. **46.** (a) 0.01238; (b) 0.09754*N*; (c) 0.9754 for 0.1*N*. **47.** (a) 0.09926*N*; (b) 0.01071. **48.** 0.003308. **49.** (a) 0.007948; (b) 0.1044*N*. **50.** (a) 0.1157*N*; (b) 0.008810.

B. Calculations in Analyses with Direct and Back Titration

1. 65.39%. 2. 60.53%. 3. 59.09%. 4. 29.08%. 5. 263.9 g. 6. 437.7 g. 7. 67.88%. 8. 98.51%. 9. 47.53%. 10. 93.24%. 11. 84.01%. 12. 59.96%. 13. 20.04%. 14. 29.99%. 15. 46.38%. 16. 98.32%. 17. 89.89%. 18. 54.50%. 19. 2.18%. 20. 0.31%. 21. 0.2%. 22. 0.7553%. 23. 79.90 g/l. 24. (a) 145.3 g/l; (b) 239.5 g/l. 25. (a) 48.74%; (b) 80.35%. 26. 98.85%.

C. Calculations in Complexometric Determinations

1. About 2.3 g. 2. About 46.5 g. 3. Accurate weight about 2 g. 4. Accurately about 0.9 g. 5. $0.1000N$; 0.002005. 6. $0.05184N$. 7. Accurately about 2.5 g of $CaCO_3$, 3.0 g of $MgSO_4$. 8. $N_{Ca} + + N_{Mg} = 0.04988N$. 9. 30.02% CaO; 19.64% MgO. 10. 2.92% Ca; 1.65% Mg. 11. 29.37% CaO; 19.52% MgO. 12. 10.21 mg/lit; 0.84 mg-equiv/lit.

APPENDIX

Two-place Logarithms for Tentative Calculations of pH, pC, pK

	0	1	2	3	4	5	6	7	8	9	
1	00	04	08	11	15	18	20	23	26	28	1
2	30	32	34	36	38	40	42	43	45	46	2
3	48	49	51	52	53	54	56	57	58	59	3
4	60	61	62	63	64	65	66	67	68	69	4
5	70	71	72	72	73	74	75	76	76	77	5
6	78	79	79	80	81	81	82	83	83	84	6
7	85	85	86	86	87	88	88	89	89	90	7
8	90	91	91	92	92	93	94	94	95	95	8
9	95	96	96	97	97	98	98	99	99		9
	0	1	2	3	4	5	6	7	8	9	

Mantissas of logarithms of frequently occurring numbers:

2	3 010
25	3 979
5	6 990

APPENDIX

Table 1

Atomic, Molecular, and Equivalent Masses of Some Substances and Their Logarithms

Compound	Mol. wt. *M*	log *M*
Ag	107.87	0329
AgBr	187.78	2737
AgSCN	165.96	2201
AgCl	143.32	1562
Ag_2CrO_4	331.73	5208
Ag_2CO_3	275.75	4406
AgI	234.77	3707
$AgNO_3$	169.88	2303
Ag_2O	231.74	3651
Ag_2S	247.80	3941
Al	26.98	4311
1/3Al	8.99	9538
2Al	53.96	7321
$Al(C_9H_6ON)_3$ (hydroxyquinolinate)	459.44	6622
Al_2O_3	101.96	0086
$1/6Al_2O_3$	16.99	2303
$Al(OH)_3$	78.00	8921
$Al_2(SO_4)_3$	342.15	5343
$Al_2(SO_4)_3 \cdot 18H_2O$	666.42	8240
As	74.92	8746
As_2O_3	197.84	2963
As_2S_3	246.04	3910
$1/4As_2O_3$	49.46	6942
As_2O_5	229.84	3613
Ba	137.34	1379
1/2Ba	68.67	8368
$BaBr_2$	297.16	4731
$BaCO_3$	197.35	2954

Table 1 (continued)

Compound	Mol. wt. M	log M
$BaCl_2$	208.25	3186
$BaCl_2 \cdot 2H_2O$	244.28	3879
$BaCrO_4$	253.33	4037
$Ba(OH)_2$	171.36	2340
$BaSO_4$	233.40	3681
$BaSO_3$	217.40	3373
B_2O_3	69.62	8429
Br	79.909	9026
C	12.011	0793
CO	28.01	4473
CO_2	44.01	6436
$1/2CO_2$	22.01	3426
Ca	40.08	6000
1/2Ca	20.04	3018
$CaCO_3$	100.09	0004
$1/2CaCO_3$	50.05	6694
CaC_2O_4	128.10	1075
$CaC_2O_4 \cdot H_2O$	146.12	1647
CaF_2	78.08	8925
$CaCl_2$	110.99	0453
$CaCl_2 \cdot 6H_2O$	219.08	3406
$Ca_3(PO_4)_2$	310.18	4916
$Ca(H_2PO_4)_2$	234.04	3693
CaO	56.08	7488
1/2CaO	28.04	4478
$Ca(OH)_2$	74.10	8698
$1/2Ca(OH)_2$	37.05	5688
$Ca(NO_3)_2$	164.09	2151
$Ca(H_2PO_4)_2 \cdot H_2$	252.06	4016
$CaSO_4$	136.14	1341
$CaSO_4 \cdot 2H_2O$	172.17	2360
$Cd_2P_2O_7$	398.74	6007
Cl	35.453	5497
2Cl	70.906	8507
C_6H_5OH	94.11	9736
Cr_2O_3	151.99	1818
$1/2Cr_2O_3$	76.01	8809
CrO_3	100.00	0000
$1/3CrO_3$	33.33	5230
$Cr(OH)_3$	103.02	0129
Cu	63.546	8031
CuSCN	121.62	0849
Cu_2O	143.08	1556
CuO	79.54	9006

Table 1 (continued)

Compound	Mol. wt. M	log M
1/2CuO	39.77	5997
$CuSO_4$	159.60	2031
$CuSO_4 \cdot 5H_2O$	249.68	3974
Fe	55.85	7470
2Fe	111.70	0479
$FeCO_3$	115.86	0641
$FeCl_2$	126.75	1030
$FeCl_3$	162.21	2101
FeO	71.85	8564
Fe_2O_3	159.69	2034
$Fe(OH)_3$	106.87	0290
$1/2Fe_2O_3$	79.85	9023
Fe_3O_4	231.54	3647
$2Fe(OH)_3$	213.74	3299
FeS	87.91	9441
$FeSO_4$	151.91	1815
$FeSO_4 \cdot 7H_2O$	278.02	4442
$Fe_2(SO_4)_3$	399.88	6020
H	1.00797	0034
H_2	2.016	3045
HO^-	17.01	2307
H_2O	18.015	2558
$1/2H_2O$	9.008	9542
$2H_2O$	36.030	5567
$3H_2O$	54.01	7328
H_2O_2	34.01	5318
H_3BO_3	61.83	7913
HCOOH	46.03	6631
CH_3COOH	60.05	7785
CH_3COO^-	59.04	7712
$H_2C_2O_4$	90.04	9544
$1/2H_2C_2O_4$	45.02	6534
$H_2C_2O_4 \cdot 2H_2O$	126.07	1007
$1/2H_2C_2O_4 \cdot 2H_2O$	63.04	7996
$1/2H_2C_4H_4O_4$ (succinic acid)	59.05	7712
C_6H_5COOH (benzoic acid)	122.13	0868
HCl	36.46	5618
2HCl	72.92	8629
HNO_3	63.01	7994
H_3PO_4	98.00	9912
H_2S	34.08	5326
H_2SO_4	98.08	9916
$1/2H_2SO_4$	49.04	6906
Hg	200.59	3023

Table 1 (continued)

Compound	Mol. wt. *M*	log *M*
Hg_2Cl_2	472.09	6740
$HgCl_2$	271.50	4338
HgO	216.59	3356
I	126.90	1035
K	39.10	5922
$KAl(SO_4)_2 \cdot 12H_2O$	474.39	6762
KBr	119.01	0755
$KBrO_3$	167.00	2227
$1/6KBrO_3$	27.83	4446
$KHCO_3$	100.11	0005
K_2CO_3	138.21	1405
$1/2K_2CO_3$	69.11	8396
KCl	74.56	8726
$KClO_3$	122.55	0885
$1/6KClO_3$	20.43	3102
K_2CrO_4	194.20	2882
$K_2Cr_2O_7$	294.19	4686
$1/6K_2Cr_2O_7$	49.03	6905
$K_3[Fe(CN)_6]$	329.23	5175
$K_4[Fe(CN)_6]$	368.33	5662
KI	166.01	2201
KIO_3	214.00	3304
$1/6KIO_3$	35.67	5523
$KMnO_4$	158.04	1987
$1/5KMnO_4$	31.61	4998
$1/3KMnO_4$	52.68	7216
K_2O	94.20	9741
$1/2K_2O$	47.10	6731
K_2PtCl_6	486.01	6867
KOH	56.11	7491
K_2SO_4	174.27	2412
Mg	24.31	3858
$MgCO_3$	84.32	9259
$Mg(NH_4)PO_4 \cdot 6H_2O$	245.43	3899
MgO	40.31	6054
$Mg(OH)_2$	58.33	7659
MgC_2O_4	112.33	0505
$MgCl_2 \cdot KCl \cdot 6H_2O$	277.86	4438
$Mg_2P_2O_7$	222.56	3476
$MgSO_4$	120.37	0806
$MgSO_4 \cdot 7H_2O$	246.48	3918
$MnCO_3$	114.95	0607
MnO_2	86.94	9392
$1/2MnO_2$	43.47	6382

Table 1 (continued)

Compound	Mol. wt. M	log M
N	14.007	1464
NH_3	17.03	2311
$2NH_3$	34.06	5323
MH_4^+	18.04	2562
$(NH_4)_2Al_2(SO_4)_4 \cdot 24H_2O$	906.66	9574
$(NH_4)_3PO_4 \cdot 12MoO_3$	1877	2735
NH_4Br	97.95	9910
NH_4SCN	76.12	8815
$(NH_4)_2C_2O_4 \cdot H_2O$	142.11	1526
$1/2(NH_4)_2C_2O_4 \cdot H_2O$	71.06	8517
NH_4Cl	53.49	7282
$NH_4Fe(SO_4)_2 \cdot 12H_2O$	482.19	6832
$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$	392.14	5935
$NH_4H_2PO_4$	115.03	0607
$(NH_4)_2PO_4$	132.06	1209
NH_4I	144.94	1611
NH_4NO_3	80.00	9031
NH_4OH	35.046	5447
$(NH_4)_2PtCl_6$	443.88	6473
$(NH_4)_2SO_4$	132.14	1212
N_2O_5	108.01	0335
Na	22.99	3615
$Na_2B_4O_7$	201.22	3038
$Na_2B_4O_7 \cdot 10H_2O$	381.37	5814
$1/2Na_2B_4O_7 \cdot 10H_2O$	190.69	2804
NaBr	102.90	0123
Na_2CO_3	105.99	0253
NaHCOO	68.02	8326
$1/2Na_2CO_3$	53.00	7243
$Na_2CO_3 \cdot 10H_2O$	286.14	4567
$1/2Na_2CO_3 \cdot 10H_2O$	143.07	1556
$Na_2C_2O_4$	134.00	1271
$1/2Na_2C_2O_4$	67.00	8261
Na_3AlF_6	209.94	3222
$NaCH_3COO$	82.03	9140
$Na_2Cr_2O_7$	261.97	4183
$1/6Na_2Cr_2O_7$	43.66	6401
$NaMg(UO_2)_3 \cdot (CH_3COO)_9$	1388.94	1427
NaCl	58.44	7667
Na_2CrO_4	161.98	2095
$NaHCO_3$	84.01	9244
$Na_2HPO_4 \cdot 12H_2O$	358.14	5541
$NaPO_3$	101.96	0085
NaI	149.89	1759

Table 1 (continued)

Compound	Mol. wt. M	log M
$NaNO_2$	69.00	8389
$NaNO_3$	85.00	9294
Na_2O	61.98	7923
$1/2Na_2O$	30.99	4913
Na_2O_2	77.98	8919
NaOH	40.00	6021
Na_2S	78.04	8923
$1/2Na_2S$	39.02	5913
$Na_2S_2O_3$	158.11	1990
$Na_2S_2O_3 \cdot 5H_2O$	248.18	3948
Na_2SO_3	126.04	1004
$1/2Na_2SO_3$	63.02	7994
$Na_2SO_3 \cdot 7H_2O$	252.15	4017
$1/2Na_2SO_3 \cdot 7H_2O$	126.08	1007
Na_2SO_4	142.04	1523
$Na_2SO_4 \cdot 10H_2O$	322.19	5082
Ni	58.71	7687
NiO	74.71	8734
$Ni(C_4N_2O_2H_7)_2$	288.94	4609
$NiSO_4 \cdot 7H_2O$	280.88	4485
O	15.9994	20412
OH^-	17.01	2307
P	30.97	4910
P_2O_5	141.98	1523
$P_2O_5 \cdot 24MoO_3$	3596.50	5559
Pb	207.19	3164
$PbBr_2$	368.01	5647
$Pb(CH_3COO)_2 \cdot 3H_2O$	379.33	5790
$PbCO_3$	267.20	4268
$PbCl_2$	278.10	4442
$PbCrO_4$	323.18	5095
PbI_2	461.00	6637
PbO	223.19	3487
Pb_3O_4	685.57	8361
PbO_2	239.19	3788
PbS	239.25	3790
$PbSO_4$	303.25	4818
Pt	195.09	2880
S	32.064	5059
SO_2	64.06	8066
SO_3	80.06	9034
SO_4^{2-}	96.06	9826
Sb	121.75	0856
Sb_2O_3	291.50	4647

Table 1 (continued)

Compound	Mol. wt. *M*	log *M*
Si	28.09	4486
SiF_4	104.08	0173
SiO_2	60.09	7788
Sn	118.69	0745
$SnCl_2$	189.60	2779
$SnCl_2 \cdot 2H_2O$	225.63	3536
SnO	134.69	1294
SnO_2	150.69	1781
Sr	87.62	9426
$SrCO_3$	147.63	1692
$Sr(OH)_2 \cdot 8H_2O$	265.76	4245
$Sr(NO_3)_2$	211.63	3255
$SrSO_4$	183.68	2641
Zn	65.37	8154
$ZnCO_3$	125.38	0982
$ZnCl_2$	136.28	1345
$ZnNH_4PO_4$	178.40	2515
ZnO	81.37	9105
$Zn(OH)_2$	99.39	9973
$Zn_2P_2O_7$	304.68	4840
$ZnSO_4 \cdot 7H_2O$	287.54	4587
ZnS	97.43	9857

Table 2

Gravimetric Factors and Their Logarithms

Substance determined	Weighing form	*F*	log *F*
Ag	AgCl	0.7526	$\bar{1}$.8766
$AgNO_3$	AgCl	1.1852	0.0738
Ag_2O	AgCl	0.8084	$\bar{1}$.9076
Al	Al_2O_3	0.5292	$\bar{1}$.7237
$Al_2(SO_4)_3$	Al_2O_3	3.3558	0.5258
Ba	$BaSO_4$	0.5885	$\bar{1}$.7697
$BaCO_3$	$BaSO_4$	0.8455	$\bar{1}$.9271
$BaCl_2$	$BaSO_4$	0.8923	$\bar{1}$.9505

Table 2 (continued)

Substance determined	Weighing form	*F*	log *F*
$BaCl_2 \cdot 2H_2O$	$BaSO_4$	1.0466	0.0198
C	CO_2	0.2729	$\bar{1}$.4360
CO_2	$CaCO_3$	0.4397	$\bar{1}$.6432
CO_2	CaO	0.7848	$\bar{1}$.8947
Ca	$CaCO_3$	0.4005	$\bar{1}$.6025
Ca	CaO	0.7147	$\bar{1}$.8541
$CaCO_3$	CO_2	2.2743	0.3569
$CaCO_3$	CaO	1.7847	0.2516
$CaCO_3$	$CaSO_4$	0.7351	$\bar{1}$.8664
$CaCl_2$	CaO	1.9793	0.2965
CaO	CO_2	1.2743	0.1052
CaO	$CaCO_3$	0.5603	$\bar{1}$.7484
$Ca_3(PO_4)_2$	CaO	$\bar{1}$.8444	0.2659
$CaSO_4$	CaO	2.4276	0.3852
Cl	AgCl	0.2474	$\bar{1}$.3933
Cu	CuO	0.7989	$\bar{1}$.9025
Cu	CuS	0.6648	$\bar{1}$.8227
CuO	Cu	1.2517	0.0975
$CuSO_4$	CuO	2.0061	0.3024
$CuSO_4 \cdot 5H_2O$	Cu	3.9297	0.5942
$CuSO_4 \cdot 5H_2O$	CuO	3.1391	0.4968
Fe	Fe_2O_3	0.6994	$\bar{1}$.8448
FeO	Fe_2O_3	0.8998	$\bar{1}$.9542
Fe_2O_3	Fe	1.4297	0.1553
FeS_2	Fe_2O_3	1.5025	0.1768
$FeSO_4 \cdot 7H_2O$	Fe	4.9782	0.6971
Fe_3O_4	Fe_2O_3	0.9666	$\bar{1}$.9853
HCl	AgCl	0.2544	$\bar{1}$.4055
H_2SO_4	$BaSO_4$	0.4202	$\bar{1}$.6235
K	K_2PtCl_6	0.1609	$\bar{1}$.2065
KCl	K_2PtCl_6	0.3068	$\bar{1}$.4868
Mg	MgO	0.6032	$\bar{1}$.7804
Mg	$Mg_2P_2O_7$	0.2185	$\bar{1}$.3395

Table 2 (continued)

Substance determined	Weighing form	*F*	log *F*
$MgCO_3$	$Mg_2P_2O_7$	0.7576	$\bar{1}.8794$
MgO	$Mg_2P_2O_7$	0.3623	$\bar{1}.5591$
Ni	NiO	0.7858	$\bar{1}.8953$
O	H_2O	0.8881	$\bar{1}.9485$
P	$Mg_2P_2O_7$	0.2783	$\bar{1}.4446$
P_2O_5	$Mg_2P_2O_7$	0.6377	$\bar{1}.8046$
Pb	$PbCrO_4$	0.6411	$\bar{1}.8069$
Pb	$PbSO_4$	0.6833	$\bar{1}.8346$
S	$BaSO_4$	0.1374	$\bar{1}.1380$
SO_3	$BaSO_4$	0.3430	$\bar{1}.5353$
Si	SiO_2	0.4672	$\bar{1}.6695$
Zn	$ZnNH_4PO_4$	0.3665	$\bar{1}.5641$
Zn	$Zn_2P_2O_7$	0.4291	$\bar{1}.6326$
$ZnCO_3$	ZnO	1.5407	0.1877
ZnO	Zn	1.2447	0.0951
ZnO	$Zn_2P_2O_7$	0.5341	$\bar{1}.7277$
ZnS	ZnO	1.1975	0.0783

Table 3

Titrimetric Factors and Their Logarithms

$$F = \frac{E_{\text{substance determined}}}{E_{\text{standard substance}}}$$

Substance determined	Standard substance	*F*	log *F*
	Redox Titrations		
$KMnO_4$	$H_2C_2O_4 \cdot 2H_2O$	0.5014	$\bar{1}.7002$
$KMnO_4$	$H_2C_2O_4$	0.7021	$\bar{1}.8464$
$KMnO_4$	$Na_2C_2O_4$	0.4718	$\bar{1}.6738$

Table 3 (continued)

Substance determined	Standard substance	*F*	log *F*
$KMnO_4$	$(NH_4)_2C_2O_4 \cdot H_2O$	0.4448	$\bar{1}.6482$
$KMnO_4$	Fe	0.5659	$\bar{1}.7527$
$H_2C_2O_4$	$KMnO_4$	1.4240	0.1535
$H_2C_2O_4 \cdot 2H_2O$	$KMnO_4$	1.9942	0.2998
$Na_2C_2O_4$	$KMnO_4$	2.1197	0.3263
$(NH_4)_2C_2O_4 \cdot H_2O$	$KMnO_4$	2.2481	0.3518
Fe	$KMnO_4$	1.7670	0.2472
$FeSO_4$	$KMnO_4$	4.8064	0.6818
Fe_2O_3	$KMnO_4$	2.5260	0.4024
$NaNO_2$	$KMnO_4$	1.0915	0.0380
Na_2SO_3	$KMnO_4$	1.9940	0.2997
$Na_2SO_3 \cdot 7H_2O$	$KMnO_4$	3.9892	0.6009
MnO_2	$Na_2C_2O_4$	0.6488	$\bar{1}.8121$
MnO_2	$(NH_4)_2C_2O_4 \cdot H_2O$	0.6118	$\bar{1}.7866$
MnO_2	$H_2C_2O_4 \cdot 2H_2O$	0.6896	$\bar{1}.8386$
Na_2SO_3	I	0.4966	$\bar{1}.6960$
$Na_2SO_3 \cdot 7H_2O$	I	0.9935	$\bar{1}.9972$
H_2S	I	0.1343	$\bar{1}.1281$
As_2O_3	I	0.3897	$\bar{1}.5907$
$Na_2S_2O_3 \cdot 5H_2O$	$K_2Cr_2O_7$	5.0613	0.7043
Cl	$Na_2S_2O_3 \cdot 5H_2O$	0.1429	$\bar{1}.1550$
I	$Na_2S_2O_3 \cdot 5H_2O$	0.5113	$\bar{1}.7087$
KIO_3 (as I)	$Na_2S_2O_3 \cdot 5H_2O$	0.1437	$\bar{1}.1575$
CrO_3	$Na_2S_2O_3 \cdot 5H_2O$	0.1343	$\bar{1}.1281$
	Acid-base Titrations		
HCl	$Na_2B_4O_7 \cdot 10H_2O$	0.1912	$\bar{1}.2815$
HCl	Na_2CO_3	0.6882	$\bar{1}.8377$
HCl	Na	1.5860	0.2004
H_2SO_4	$Na_2B_4O_7 \cdot 10H_2O$	0.2571	$\bar{1}.4101$
H_2SO_4	Na_2CO_3	0.9253	$\bar{1}.9663$
H_2SO_4	Na	2.1325	0.3289

Table 3 (continued)

Substance determined	Standard substance	*F*	log *F*
KOH	$H_2C_2O_4 \cdot 2H_2O$	0.8902	$\bar{1}.9495$
NaOH	$H_2C_2O_4 \cdot 2H_2O$	0.6346	$\bar{1}.8025$
SO_3	KOH	0.7135	$\bar{1}.8534$
SO_3	NaOH	1.0008	0.0003
KOH	HCl	1.5387	0.1872
KOH	H_2SO_4	1.1442	0.0585
K_2O	HCl	1.2916	0.1111
K_2O	H_2SO_4	0.9604	$\bar{1}.9825$
NaOH	HCl	1.0969	0.0402
NaOH	H_2SO_4	0.8156	$\bar{1}.9115$
Na_2O	HCl	0.8499	$\bar{1}.9294$
Na_2O	H_2SO_4	0.6320	$\bar{1}.8007$

Table 4

Dissociation Constants of Some Weak Electrolytes

Electrolyte	Dissociation constant	*K* at 25 °C
Water	$K = \frac{[H^+]\,[OH^-]}{[H_2O]}$	1.8×10^{-16}
	Mineral acids	
Acetic	$K = \frac{[H^+]\,[NO_2^-]}{[HNO_2]}$	4.5×10^{-4}
Boric	$K_1 = \frac{[H^+]\,[H_2BO_3^-]}{[H_3BO_3]}$	6×10^{-10}
Sulphurous	$K_1 = \frac{[H^+]\,[HSO_3^-]}{[H_2SO_3]}$	1.2×10^{-2}
	$K_2 = \frac{[H^+]\,[SO_3^{2-}]}{[HSO_3^-]}$	1.0×10^{-7}
Hydrosulphuric	$K_1 = \frac{[H^+]\,[HS^-]}{[H_2S]}$	1.08×10^{-7}
	$K_2 = \frac{[H^+]\,[S^{2-}]}{[HS^-]}$	1.0×10^{-15}

Table 4 (continued)

Electrolyte	Dissociation constant	K at 25 °C
Hydrocyanic	$K = \frac{[H^+]\,[CN^-]}{[HCN]}$	7.2×10^{-10}
Carbonic	$K_1 = \frac{[H^+]\,[HCO_3^-]}{[H_2CO_3]}$	4.3×10^{-7}
	$K_2 = \frac{[H^+]\,[CO_3^{2-}]}{[HCO_3^-]}$	5.6×10^{-11}
Phosphoric	$K_1 = \frac{[H^+]\,[H_2PO_4^-]}{[H_3PO_4]}$	1.1×10^{-2}
	$K_2 = \frac{[H^+]\,[HPO_4^{2-}[}{[H_2PO_4^{2-}]}$	2.0×10^{-7}
	$K_3 = \frac{[H^+]\,[PO_4^{3-}]}{[HPO_4^{2-}]}$	0.9×10^{-12}
	Organic acids	
Tartaric	$K_1 = \frac{[H^+]\,[HC_4H_4O_6^-]}{[H_2C_4H_4O_6]}$	1.04×10^{-3}
	$K_2 = \frac{[H^+]\,[C_4H_4O_6^{2-}]}{[HC_4H_4O_6^-]}$	4.55×10^{-5}
Formic	$K = \frac{[H^+]\,[HCOO^-]}{[HCOOH]}$	1.77×10^{-4}
Acetic	$K = \frac{[H^+]\,[CH_3COO^-]}{[CH_3COOH]}$	1.86×10^{-5}
Oxalic	$K_1 = \frac{[H^+]\,[HC_2O_4^-]}{[H_2C_2O_4]}$	5.9×10^{-2}
	$K_2 = \frac{[H^+]\,[C_2O_4^{2-}]}{[HC_2O_4^-]}$	6.4×10^{-5}
	Bases	
Ammonium hydroxide	$K = \frac{[NH_4^+]\,[OH^-]}{[NH_4OH]}$	1.79×10^{-5}

Table 5

Degree of Dissociation of Acids, Bases, and Salts in Aqueous Solutions

Electrolyte	Formula	Degree of dissociation, %	
		in 1*N* soln	in 0.1*N* soln
	Acids		
Nitric	HNO_3	82	92
Hydrochloric	HCl	78	91
Hydrobromic	HBr	—	90
Hydriodic	HI	—	90
Sulphuric	H_2SO_4	51	58
Oxalic	$H_2C_2O_4$	—	31
Phosphoric	H_3PO_4	—	26
Sulphurous	H_2SO_3	—	20
Hydrofluoric	HF	—	15
Tartaric	$H_2C_4H_4O_6$	—	13
Acetic	CH_3COOH	0.4	1.3
Carbonic	H_2CO_3	—	0.17
Hydrosulphuric	H_2S	—	0.07
Boric	H_3BO_3	—	0.01
Hydrocyanic	HCN	—	0.007
	Bases		
Potassium hydroxide	KOH	77	89
Sodium hydroxide	NaOH	73	84
Ammonium hydroxide	NH_4OH	0.4	1.3
	Salts		
Me^+A^- (e.g. KCl)		—	86
$Me_2^+A^{2-}$ and $Me^{2+}A_2^-$ (e.g. K_2SO_4, $BaCl_2$)		—	73
$Me_3^+A^{3-}$ or $Me^{3+}A_3^-$ (e.g. K_3PO_4, $AlCl_3$)		—	65
$Me^{2+}A^{2-}$ (e.g. $CuSO_4$)		—	40

Notes: 1. Apparent degrees of dissociation are given for strong electrolytes (determined by the electric conductivity of solutions).
2. First step dissociations are given for di- and polybasic acids.
3. Degrees of dissociation of various salts of the same type strongly differ in uninormal solutions. They are not therefore given in the Table. Data for some of them are given here: KCl, 75%; NaCl, 67%; KNO_3, 64%; CH_3COONa, 63%; K_2SO_4, 53%; Na_2SO_4, 45%, etc.

Table 6

Solubility Products of Some Sparingly Soluble Electrolytes (at 25 °C)

Electrolyte	SP	Electrolyte	SP
CuCl	1.4×10^{-6}	CdS	1.2×10^{-28}
CuBr	4.1×10^{-8}	$CdCO_3$	1.82×10^{-14}
CuI	1.1×10^{-12}	$Ba(OH)_2$	2.2×10^{-1}
Cu_2S	2.6×10^{-49}	$BaCO_3$	4.93×10^{-9}
CuS	3.2×10^{-38}	$BaSO_4$	9.9×10^{-11}
$CuCO_3$	2.36×10^{-10}	BaC_2O_4	1.7×10^{-7}
CuC_2O_4	2.9×10^{-8}	$BaCrO_4$	2.3×10^{-10}
AgOH	2.0×10^{-8}	$Ba_3(PO_4)_2$	1.5×10^{-28}
AgCl	1.7×10^{-10}	Hg_2Cl_2	2.0×10^{-18}
AgBr	3.3×10^{-13}	Hg_2Br_2	1.3×10^{-21}
AgI	8.5×10^{-17}	Hg_2I_2	1.2×10^{-28}
Ag_2S	5.9×10^{-52}	Hg_2CO_3	9.0×10^{-17}
Ag_2CO_3	8.15×10^{-12}	HgS	4.0×10^{-53}
$Ag_2C_2O_4$	5.0×10^{-12}	$Al(OH)_3$	1.1×10^{-15}
Ag_2CrO_4	2.0×10^{-12}	SnS	1.0×10^{-27}
$Ag_2Cr_2O_7$	2.0×10^{-7}	$PbCl_2$	1.7×10^{-5}
Ag_2SO_4	6.0×10^{-6}	$PbBr_2$	6.3×10^{-6}
Ag_3PO_4	1.8×10^{-16}	PbI_2	8.7×10^{-9}
Ag_3AsO_4	1.0×10^{-19}	PbS	6.8×10^{-29}
AgSCN	1.2×10^{-12}	$PbCO_3$	7.24×10^{-14}
$Mg(OH)_2$	5.5×10^{-12}	$PbSO_4$	1.8×10^{-8}
$MgCO_3$	1.0×10^{-5}	PbC_2O_4	3.4×10^{-11}
MgC_2O_4	8.6×10^{-5}	$PbCrO_4$	1.8×10^{-14}
$MgNH_4PO_4$	2.5×10^{-13}	$Pb_3(PO_4)_2$	1.5×10^{-32}
$Ca(OH)_2$	2.2×10^{-2}	As_2S_3	4.1×10^{-29}
$CaCO_3$	1.7×10^{-8}	Sb_2S_3	2.9×10^{-59}
$CaSO_4$	6.26×10^{-5}	$Mn(OH)_2$	4.0×10^{-14}
CaF_2	4×10^{-11}	MnS	1.1×10^{-15}
CaC_2O_4	3.8×10^{-9}	$MnCO_3$	5.05×10^{-10}
$CaCrO_4$	2.3×10^{-2}	$Fe(OH)_2$	1.65×10^{-15}
$Ca_3(PO_4)_2$	1.2×10^{-14}	FeS	3.8×10^{-20}
$Zn(OH)_2$	4.5×10^{-17}	$FeCO_3$	2.11×10^{-11}
ZnS	7.4×10^{-27}	$Fe(OH)_3$	4.0×10^{-38}
$ZnCO_3$	9.98×10^{-11}	$Co(OH)_2$	1.6×10^{-18}
$Sr(OH)_2$	6.7×10^{-2}	CoS	3.1×10^{-23}
$SrCO_3$	9.42×10^{-10}	$CoCO_3$	1.45×10^{-13}
$SrCO_4$	3.6×10^{-7}	$Ni(OH)_2$	8.7×10^{-19}
SrC_2O_4	5.6×10^{-8}	NiS	1.4×10^{-24}
$SrCrO_4$	3.6×10^{-5}	$NiCO_3$	1.35×10^{-7}

Table 7

Instability Constants of Some Complex Ions

Dissociation of Complex	Instability constant
$[AgCl_2]^- \rightleftarrows Ag^+ + 2Cl^-$	2.3×10^{-6}
$[Ag(NH_3)_2]^+ \rightleftarrows Ag^+ + 2NH_3$	7.2×10^{-8}
$[AgS_2O_3]^- \rightleftarrows Ag^+ + S_2O_3^{2-}$	1.0×10^{-13}
$[Ag(CN)_2]^- \rightleftarrows Ag^+ + 2CN^-$	1×10^{-21}
$[CuCl_4]^{2-} \rightleftarrows Cu^{2+} + 4Cl^-$	2.4×10^{-6}
$[Cu(NH_3)_4]^{2+} \rightleftarrows Cu^{2+} + 4HN_3$	2.1×10^{-13}
$[Cu(CH)_4]^{2-} \rightleftarrows Cu^{2+} + 4CN^-$	5×10^{-28}
$[Zn(NH_3)_4]^{2+} \rightleftarrows Zn^{2+} + 4NH_3$	3.5×10^{-10}
$[Zn(CN)_4]^{2-} \rightleftarrows Zn^{2+} + 4CN^-$	2×10^{-17}
$[Cd(NH_3)_4]^{2+} \rightleftarrows Cd^{2+} + 4NH_3$	1×10^{-7}
$[Cd(CN)_4]^{2-} \rightleftarrows Cd^{2+} + 4CN^-$	1.4×10^{-17}
$[HgCl_4]^{2-} \rightleftarrows Hg^{2+} + 4Cl^-$	6×10^{-17}
$[HgBr_4]^{2-} \rightleftarrows Hg^{2+} + 4Br^-$	2.2×10^{-22}
$[HgI_4]^{2-} \rightleftarrows Hg^{2+} + 4I^-$	5×10^{-31}
$[Hg(CN)_4]^{2-} \rightleftarrows Hg^{2+} + 4CN^-$	4×10^{-42}
$[Fe(CN)_6]^{4-} \rightleftarrows Fe^{2+} + 6CN^-$	2×10^{-37}
$[Fe(CN)_6]^{3-} \rightleftarrows Fe^{3+} + 6CN^-$	1×10^{-44}
$[Co(NH_3)_6]^{2+} \rightleftarrows Co^{2+} + 6NH_3$	7.8×10^{-6}
$[Co(NH_3)_6]^{3+} \rightleftarrows Co^{3+} + 6NH_3$	6.2×10^{-36}
$[Ni(NH_3)_6]^{2+} \rightleftarrows Ni^{2+} + 6NH_3$	1.8×10^{-9}

Table 8

Normal Potentials of Some Redox Systems

Reduced form	Oxidized form	Normal potential, *V*	Reduced form	Oxidized form	Normal potential, *V*
Li	Li^+	−3.02	Cr^{3+}	CrO_7^{2-}	−0.12*
Ca	Ca^{2+}	−2.87	H_2	$2H^+$	0
Zn	Zn^{2+}	−0.76	H_2S	S	+0.141
$H_2C_2O_4$	CO_2	−0.49	Sn^{2+}	Sn^{4+}	+0.15
Fe	Fe^{2+}	−0.44	$S_2O_3^{2-}$	$S_4O_6^{2-}$	+0.17

Table 8 (continued)

Reduced form	Oxidized form	Normal potential, *V*	Reduced form	Oxidized form	Normal potential, *V*
SO_3^{2-}	SO_4^{2-}	+0.20	$2Br^-$	Br_2	+1.065
Cu	Cu^{2+}	+0.34	I^-	IO_3^-	+1.085
S	SO_3^{2-}	+0.45	Cr^{3+}	$Cr_2O_7^{2-}$	+1.36
I^-	$1/21_2$	+0.53	Cl^-	$1/2Cl_2$	+1.36
MnO_4^{2-}	MnO_4^-	+0.54	Mn^{2+}	MnO_4^-	+1.52
H_2O_2	O_2+2H^+	+0.662	$2F^-$	F_2	+2.85
Fe^{2+}	Fe^{3+}	+0.771			

* In an alkaline medium

Table 9

Densities and Percent Composition of Solutions of Acids and Alkalis

Density of KOH and NaOH solutions

Mass, %	Density		Mass, %	Density	
	KOH	NaOH		KOH	NaOH
1	1.008	1.010	19	1.179	—
2	1.018	1.021	20	1.188	1.219
3	1.027	1.032	21	1.198	—
4	1.036	1.043	22	1.208	1.241
5	1.045	1.054	23	1.218	—
6	1.051	1.065	24	1.229	1.263
7	1.064	1.076	25	1.239	—
8	1.073	1.087	26	1.249	1.285
9	1.082	1.098	27	1.259	—
10	1.092	1.109	28	1.270	1.306
11	1.101	—	29	1.280	—
12	1.111	1.131	30	1.291	1.328
13	1.120	—	31	1.301	—
14	1.130	1.153	32	1.312	1.349
15	1.140	—	33	1.322	—
16	1.149	1.175	34	1.333	1.370
17	1.159	—	35	1.344	—
18	1.169	1.197	36	1.355	1.390

Table 9 (continued)

Mass, %	Density		Mass, %	Density	
	KOH	NaOH		KOH	NaOH
37	1.366	—	45	1.456	—
38	1.377	1.410	46	1.467	1.487
39	1.388	—	47	1.479	—
40	1.399	1.430	48	1.491	1.507
41	1.410	—	49	1.503	—
42	1.421	1.449	50	1.514	1.525
43	1.433	—	51	1.526	—
44	1.444	1.469	52	1.538	—

Density of Strong Acid Solutions

Mass, %	Density			Mass, %	Density		
	HCl	H_2SO_4	HNO_3		HCl	H_2SO_4	HNO_2
1	1.003	1.005	1.004	25	—	1.178	1.147
2	1.008	1.012	1.009	26	1.129	1.186	1.153
3	—	1.018	1.015	27	—	1.194	1.160
4	1.018	1.025	1.020	28	1.139	1.202	1.167
5	—	1.032	1.026	29	—	1.210	1.173
6	1.028	1.038	1.031	30	1.149	1.219	1.180
7	—	1.045	1.037	31	—	1.227	1.187
8	1.038	1.052	1.043	32	1.159	1.235	1.193
9	—	1.059	1.049	33	—	1.243	1.200
10	1.047	1.066	1.054	34	1.169	1.252	1.207
11	—	1.073	1.060	35	—	1.260	1.214
12	1.057	1.080	1.066	36	1.179	1.268	1.221
13	—	1.087	1.072	37	—	1.277	1.227
14	1.068	1.095	1.078	38	1.189	1.286	1.234
15	—	1.102	1.084	39	—	1.294	1.240
16	1.078	1.109	1.090	40	1.198	1.303	1.246
17	—	1.117	1.096	41		1.312	1.253
18	1.088	1.124	1.103	42		1.321	1.259
19	—	1.132	1.109	43		1.329	1.266
20	1.098	1.139	1.115	44		1.338	1.272
21	—	1.147	1.121	45		1.348	1.278
22	1.108	1.155	1.128	46		1.357	1.285
23	—	1.163	1.134	47		1.366	1.291
24	1.119	1.170	1.140	48		1.376	1.298

Table 9 (continued)

Mass, %	Density			Mass, %	Density		
	HCl	H_2SO_4	HNO_3		HCl	H_2SO_4	HNO_3
49		1.385	1.304	75		1.669	1.434
50		1.395	1.310	76		1.681	1.438
51		1.405	1.316	77		1.693	1.441
52		1.415	1.322	78		1.704	1.445
53		1.425	1.328	79		1.716	1.449
54		1.435	1.334	80		1.727	1.452
55		1.445	1.339	81		1.738	1.456
56		1.456	1.345	82		1.749	1.459
57		1.466	1.351	83		1.759	1.462
58		1.477	1.356	84		1.769	1.466
59		1.488	1.361	85		1.779	1.469
60		1.498	1.367	86		1.787	1.472
61		1.509	1.372	87		1.795	1.475
62		1.520	1.377	88		1.802	1.477
63		1.531	1.382	89		1.809	1.480
64		1.542	1.387	90		1.814	1.483
65		1.553	1.391	91		1.819	1.485
66		1.565	1.396	92		1.824	1.487
67		1.576	1.400	93		1.828	1.489
68		1.587	1.405	94		1.831	1.491
69		1.599	1.409	95		1.834	1.493
70		1.611	1.413	96		1.836	1.495
71		1.622	1.418	97		1.836	1.497
72		1.634	1.422	98		1.836	1.501
73		1.646	1.426	99		1.834	1.506
74		1.657	1.430	100		1.831	1.513

Density of Acetic Acid Solutions

Mass, %	Density	Mass, %	Density	Mass, %	Density
0	0.998	8	1.010	16	1.021
1	1.000	9	1.011	17	1.022
2	1.001	10	1.013	18	1.024
3	1.002	11	1.014	19	1.025
4	1.004	12	1.015	20	1.026
5	1.006	13	1.017	21	1.028
6	1.007	14	1.018	22	1.029
7	1.008	15	1.020	23	1.030

Table 9 (continued)

Mass, %	Density	Mass, %	Density	Mass, %	Density
24	1.031	50	1.058	76	1.070
25	1.033	51	1.058	77	1.070
26	1.034	52	1.059	78	1.070
27	1.035	53	1.060	79	1.070
28	1.036	54	1.060	80	1.070
29	1.037	55	1.061	81	1.070
30	1.038	56	1.062	82	1.070
31	1.040	57	1.062	83	1.070
32	1.041	58	1.063	84	1.069
33	1.042	59	1.064	85	1.069
34	1.043	60	1.064	86	1.069
35	1.044	61	1.065	87	1.068
36	1.045	62	1.065	88	1.068
37	1.046	63	1.066	89	1.067
38	1.047	64	1.066	90	1.066
39	1.048	65	1.067	91	1.065
40	1.049	66	1.067	92	1.064
41	1.050	67	1.068	93	1.063
42	1.051	68	1.068	94	1.062
43	1.052	69	1.068	95	1.061
44	1.053	70	1.069	96	1.059
45	1.053	71	1.069	97	1.057
46	1.054	72	1.069	98	1.055
47	1.055	73	1.069	99	1.052
48	1.056	74	1.069	100	1.050
49	1.057	75	1.070		

Density of Ammonia Solutions

Mass, %	Density	Mass, %	Density
1	0.994	16	0.936
2	0.990	18	0.930
4	0.981	20	0.923
6	0.973	22	0.916
8	0.965	24	0.910
10	0.958	26	0.904
12	0.950	28	0.898
14	0.943	30	0.892

Table 10

Calibrating Volumetric Mass of Water

A glass vessel of precisely one litre capacity at 20°C contains at the temperature $t°$ m_{20} grams of water weighed in air with brass weights.

t	$\frac{m_{20}}{1000}$	t	$\frac{m_{20}}{1000}$	t	$\frac{m_{20}}{1000}$	t	$\frac{m_{20}}{1000}$
0	0.99831	16.0	0.99781	20.8	0.99702	25.4	0.99604
1	0.99840	16.2	0.99778	21.0	0.99699	25.6	0.99600
2	0.99846	16.4	0.99776	21.2	0.99695	25.8	0.99595
3	0.99851	16.6	0.99773	21.4	0.99691	26.0	0.99590
4	0.99854	16.8	0.99770	21.6	0.99687	26.2	0.99585
5	0.99856	17.0	0.99767	21.8	0.99683	26.4	0.99580
6	0.99856	17.2	0.99764	22.0	0.99679	26.6	0.99575
7	0.99855	17.4	0.99761	22.2	0.99675	26.8	0.99570
8	0.99852	17.6	0.99758	22.4	0.99671	27.0	0.99565
9	0.99848	17.8	0.99755	22.6	0.99666	27.2	0.99560
10	0.99842	18.0	0.99751	22.8	0.99662	27.4	0.99555
11	0.99835	18.2	0.99748	23.0	0.99658	27.6	0.99550
12	0.99827	18.4	0.99745	23.2	0.99654	27.8	0.99545
13	0.99817	18.6	0.99742	23.4	0.99649	28.0	0.99540
14	0.99806	18.8	0.99738	23.6	0.99645	28.2	0.99535
14.2	0.99804	19.0	0.99735	23.8	0.99641	28.4	0.99529
14.4	0.99802	19.2	0.99731	24.0	0.99636	28.6	0.99524
14.6	0.99799	19.4	0.99728	24.2	0.99632	28.8	0.99519
14.8	0.99797	19.6	0.99724	24.4	0.99627	29.0	0.99514
15.0	0.99794	19.8	0.99721	24.6	0.99623	29.2	0.99508
15.2	0.99792	20.0	0.99717	24.8	0.99618	29.4	0.99503
15.4	0.99789	20.2	0.99714	25.0	0.99614	29.6	0.99497
15.6	0.99787	20.4	0.99710	25.2	0.99609	29.8	0.99492
15.8	0.99784	20.6	0.99706				

Logarithms

	0	1	2	3	4	5	6	7	8	9	Proportional parts								
											1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13

Table 11 (continued)

	0	1	2	3	4	5	6	7	8	9	Proportional parts								
											1	2	3	4	5	6	7	8	9
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5460	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	6775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6949	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8

Table 11 (continued)

	0	1	2	3	4	5	6	7	8	9	Proportional parts								
											1	2	3	4	5	6	7	8	9
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5

Table 11 (continued)

	0	1	2	3	4	5	6	7	8	9	Proportional parts								
											1	2	3	4	5	6	7	8	9
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

Antilogarithms

Logarithms	0	1	2	3	4	5	6	7	8	9	Proportional parts								
											1	2	3	4	5	6	7	8	9
,00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
,01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
,02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
,03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
,04	1096	1099	1102	1004	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
,05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
,06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
,07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
,08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
,09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	2
,10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	2
,11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
,12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
,13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
,14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
,15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
,16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
,17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
,18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
,19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3

Table 12 (continued)

Logarithms	0	1	2	3	4	5	6	7	8	9	Proportional parts								
											1	2	3	4	5	6	7	8	9
,20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
,21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
,22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
,23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
,24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
,25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
,26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
,27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
,28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
,29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
,30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
,31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
,32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
,33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
,34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
,35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
,36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
,37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
,38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
,39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5

Table 12 (continued)

Logarithms	0	1	2	3	4	5	6	7	8	9	Proportional parts								
											1	2	3	4	5	6	7	8	9
,40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
,41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
,42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
,43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
,44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
,45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
,46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
,47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
,48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
,49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6
,50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
,51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
,52	3311	3319	3327	3344	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
,53	3388	3396	3404	3412	3420	3428	3426	3443	3451	3459	1	2	2	3	4	5	6	6	7
,54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
,55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
,56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
,57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
,58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
,59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8

Table 12 (continued)

Logarithms	0	1	2	3	4	5	6	7	8	9	Proportional parts								
											1	2	3	4	5	6	7	8	9
,60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
,61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
,62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
,63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
,64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
,65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
,66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
,67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
,68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
,69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
,70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
,71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
,72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
,73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
,74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
,75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
,76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
,77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
,78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
,79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13

Logarithms	0	1	2	3	4	5	6	7	8	9	Proportional parts								
											1	2	3	4	5	6	7	8	9
,80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
,81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
,82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
,83	6861	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
,84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
,85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
,86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
,87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
,88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
,89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
,90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
,91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
,92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
,93	8511	8531	8551	8570	8590	8610	8633	8650	8670	8690	2	4	6	8	10	12	14	16	18
,94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
,95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
,96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
,97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
,98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
,99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20